

# 7

## **Remediation of Organic Chemicals in the Vadose Zone**

**Larry Murdoch**

**Contributors: J.S. Girke, J. Rossabi, J. Reed, D. Conley, J. Phelan, R.W. Falta, W. Heath, T.C. Hazen, R.L. Siegrist, O.R. West, M.A. Urynowicz, W.W. Slack, P. Bishop, V. Hebatpuria, L.E. Erickson, L.C Davis, and P.A. Kulakow**

### **INTRODUCTION**

The remediation of organic chemicals in the vadose zone has been blessed by remarkable success, but it has also been cursed by challenges to even our most advanced capabilities. This spectrum of outcomes to the remedial process is a result of the diversity of conditions encountered at contaminated sites. Organic chemicals are rarely stored or intentionally placed beneath the water table, so the source of most organic contamination is at the ground surface or in the shallow vadose zone. As a result, nearly all sites containing organic contaminants have at least some problems in the vadose zone, and commonly the greatest concentrations of contaminants occur in the vadose zone near the source.

The large number of sites requiring vadose zone remediation presents a broad range of conditions and circumstances, including factors related to geologic conditions, properties of the contaminants, and the ability to access the subsurface. All are critical to the performance of the remedial technique, and currently no single technique addresses all the factors found at contaminated sites. Instead, an array of techniques has been developed, some to target widespread problems and others to address the more difficult niches.

The development of soil vapor extraction (SVE) in the mid-to-late 1980s provided a method that can significantly reduce the mass of volatile compounds at sites underlain by relatively dry, sandy sediments, in areas readily accessed by conventional drilling. A significant number of sites meet those criteria, and SVE has been used to close many of them. SVE is widely available and, along with several companion techniques, it forms the backbone of our organic chemical remediation capabilities.

A variety of conditions impede SVE performance. Organic contaminants may partition into the vapor phase only sparingly, or the underlying material may be tight or marked by significant heterogeneities, or the contaminated region may be beyond the influence of conventional wells. These factors reduce the effectiveness of SVE, delaying the completion of remediation and increasing costs.

Performance improvement and cost reduction motivated the development of at least a dozen other technologies for remediating organic chemicals in the vadose zone. Each of these innovative technologies either stretches the limitations caused by geology, contaminant properties, or access, or reduces the equipment and operating costs of conventional SVE. Some are designed to improve SVE performance itself, for example, by heating the ground to accelerate the contaminant evaporation and increase the recovery rate. Others draw on different physical or chemical processes for remediation.

Contaminant recovery is by no means the only remediation method for the vadose zone. Bioremediation of hydrocarbons has been widespread and successful in many vadose settings. Other possibilities include chemically altering contaminants to benign compounds, or injecting chemicals to markedly reduce the mobility of contaminants and limit their ability to migrate to potential receptors. At some sites, naturally occurring processes may reduce the concentrations of contaminants so that subsurface monitoring is sufficient to ensure remediation.

The purpose of this chapter is to identify the current state of our capability to remediate organic chemicals in the vadose zone. The first part of the chapter describes the remedial technologies that are currently available. The second part of the chapter compares the performance of these technologies under a variety of conditions at contaminated sites. Most of the remediation methods considered here fall unambiguously into one of four major classes of remedial methods: recovery, destruc-

tion, immobilization, and natural processes, and the chapter is organized around these classes. However, a few of the technologies are capable of more than one type of action; for example, heating the subsurface will improve recovery but it can also destroy some contaminants by oxidation or pyrolysis.

All of the technologies described in the following pages have advanced through the development process and are now offered as a service by private companies. Some are widely available, while other methods are more specialized. A variety of other methods currently show promise in the laboratory, and it is expected that they will soon be added to the list of commercially available techniques.

## REMEDICATION TECHNOLOGIES

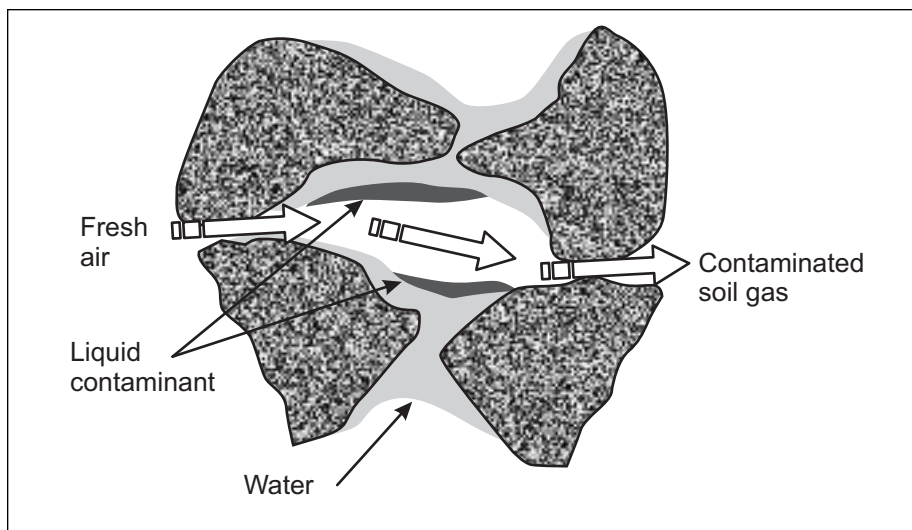
### CONVENTIONAL VAPOR EXTRACTION\*

Soil vapor extraction (SVE) is the benchmark process for remediation in the vadose zone. Its widespread application since it was developed in the 1980s is probably responsible for cleaning up more sites than any other *in situ* remedial method. SVE is achieved by inducing air flow through the contaminated zone (Figure 7-1) to extract the contaminant-laden vapors and promote vaporization/volatilization and subsequent removal of liquid, dissolved, and sorbed contaminants. The pore-scale situation depicted in Figure 7-1 can occur wherever air flow can be maintained in the subsurface. Subsurface air flow is induced in a manner analogous to pumping groundwater: vacuum blowers attached to SVE vents serve the same purpose as pumps in water wells and reduce pressures in extraction vents. SVE extraction vents resemble water wells completed in the vadose zone. Air flows downward from the ground surface towards the lower pressure in the extraction vents. Subsurface flow could likewise be induced by injecting air under pressures greater than atmospheric, but applying negative pressures (suction) allows the contaminated vapors to be captured and treated.

The subsurface flow of gases can be analyzed using a continuity equation with Darcy's law to relate volumetric flux to potential gradient,

---

\*This section was contributed by J.S. Gierke.



**Figure 7-1.** Grain-scale view of soil vapor extraction process: fresh air drawn into contaminated zone under induced vacuum displaces soil gas previously equilibrated with the contaminant, causing vaporization/volatilization of liquid, dissolved, and sorbed contaminants, potentially until chemical equilibrium is achieved. The soil gas becomes progressively more contaminated and eventually is extracted and treated.

and the ideal gas law to describe the equation of state (see Chapters 1, 3, and 5; Jordan *et al.* 1995). Because gas density is small, the gravitational component of the fluid potential is typically ignored and flow is induced primarily by pressure gradients. Analytical solutions exist for idealized flow conditions (such as homogeneous, steady-state, and axisymmetric) in either one- or two-dimensional configurations (Johnson *et al.* 1990a; Shan *et al.* 1992; Falta 1996). Numerical models account for non-ideal flow geometries and heterogeneities. By ignoring compositional effects on gas density and viscosity, and linearizing the gas flow equation, groundwater flow models can be used to simulate air flow induced by SVE (Baehr and Joss 1995).

The SVE contaminant removal process can be analyzed using a continuity equation approach with phase-partitioning (Henry's law for air-water, Raoult's law for NAPL-air and NAPL-water, and linear sorption)

between the organic, aqueous, gaseous, and sorbed phases (see Chapters 1 and 5; Baehr and Hoag 1988). Nonequilibrium mass transfer is important for chemical removal at a range of scales (Hiller and Gudemann 1989; Brusseau 1991; Gierke *et al.* 1992; Armstrong *et al.* 1994). Different stages of the removal process are characterized according to the dominant mechanisms: initially, removal is dominated by advection, which later transitions to diffusion-dominant (nonequilibrium) removal (Jordan *et al.* 1995). The advection-dominant phase is shorter as the degree of heterogeneity (in either the contaminant distribution or soil permeability) increases.

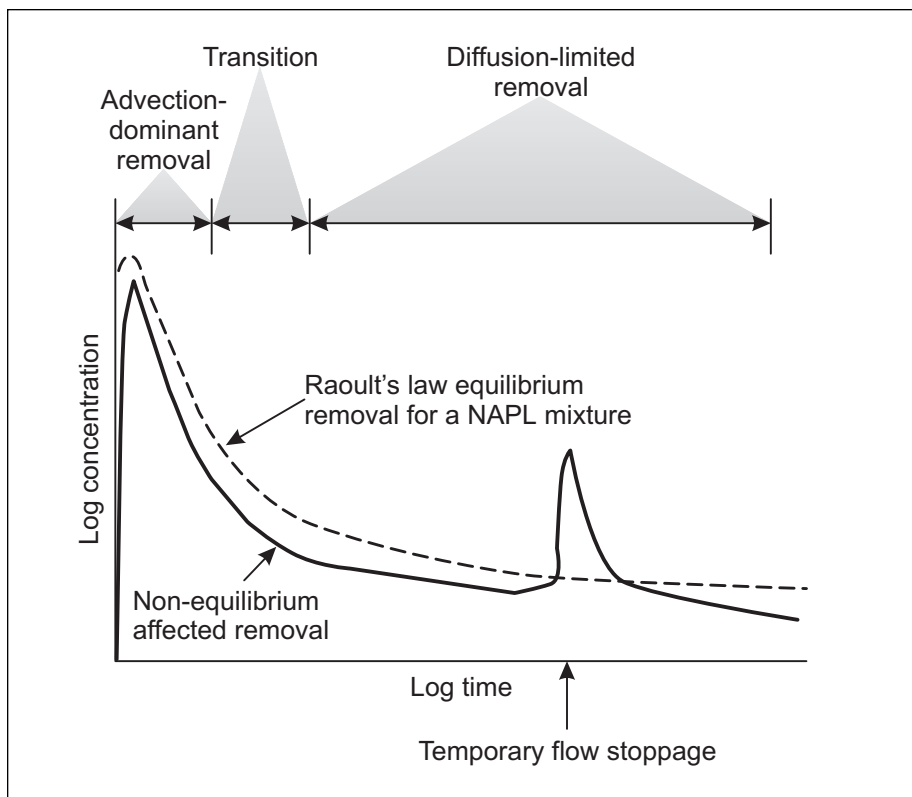
The effectiveness of SVE in removal of vadose zone contamination is due to the volatility of the contaminants, and the gas permeability of the contaminated soil. SVE also enhances *in situ* biodegradation of many organic contaminants, especially petroleum hydrocarbons. Biodegradation associated with induced air flow (*bioventing*) is discussed in more detail later.

### Contaminant Volatility

The property of volatility is characterized by the pure vapor pressure of a contaminant present as a nonaqueous phase liquid (NAPL), or by the Henry's constant if it is present only in dissolved and sorbed phases. Vapor pressure can be translated in terms of the carrying capacity of the gas phase of the contaminant. For example, a compound with a vapor pressure of 0.1-mm Hg at 25°C can achieve a vapor concentration up to 5.4 micromoles per liter of air, corresponding to the minimum vapor pressure for which SVE is practical (Hutzler *et al.* 1989). However, this lower limit of vapor pressure may be optimistic because the maximum concentration is rarely reached in field applications for reasons described below.

When contamination is present as a NAPL mixture, the capacity of the vapor phase for each contaminant is reduced to an amount directly proportional to its mole fraction in the NAPL phase (Chapter 1). Johnson *et al.* (1990a) discuss applications of Raoult's law to SVE performance. The contaminant removal observed by monitoring the SVE offgas may appear similar to the hypothetical curve shown in Figure 7-2.

The volatilization of a compound from the aqueous phase is primarily a function of its Henry's constant, which depends on the compound



**Figure 2.** Characteristic offgas concentrations observed during SVE in conventional configurations in permeable soils with NAPL contamination. Adapted from Hiller and Gudemann (1989) and Johnson *et al.* (1990a).

vapor pressure and aqueous solubility. In general, compounds with what is considered sufficiently high vapor pressure usually also have a high enough Henry's constant for SVE to be effective, that is, greater than 1 L atm/mole. (Jordan *et al.* 1995). Notable exceptions are miscible organic compounds, such as many alcohols, phenol, and acetone, all of which have high vapor pressures (greater than 80 mm Hg) but low Henry's constants (less than 0.04 L atm/mole) due to their high solubility in water.

Mixtures of dissolved contaminants increase, slightly, the volatility of most of the individual constituents, as their solubilities often decrease in the presence of other compounds. This effect is minimal and exceptions

exist when substances (such as surfactants or cosolvents) are present that increase solubility.

Contamination is always present in a heterogeneous distribution. Moreover, air flow follows the paths of least resistance (such as the shortest distance or highest permeability). Therefore, not all of the induced air flow will contact contamination. This bypassing of the contamination leads to offgas concentrations that are lower than the ideal concentration based on equilibrium calculations as illustrated in Figure 7-2. Grain-scale mass transfer processes also cause concentrations to be lower than equilibrium values. Both causes will result in abrupt increases in offgas concentrations when SVE flow is interrupted. From a practical view, differentiation between causes of nonequilibrium is unnecessary, but it remains an area of active research for development and testing of mathematical models for SVE performance prediction.

## Permeability

Permeability is the key factor determining whether a sufficient vapor flow for practical achievement of cleanup goals can be achieved. In SVE operations, soil permeability is the ability of air to flow through the vadose zone. Gas density and viscosity also affect gas flow, but to a much lesser extent for typical SVE applications (Johnson *et al.* 1990a; Falta *et al.* 1989). Gas permeabilities are a complex function of gas-filled porosity and pore size distribution. The gas permeability is the product of the intrinsic permeability,  $k$ , and the gas phase relative permeability,  $k_{rg}$ . In the vast majority of SVE projects, gas permeabilities are estimated *in situ* by applying suction to a venting well, much like aquifer permeabilities use pumping tests.

The minimum level of soil-gas permeability at which SVE is practical is difficult to establish because it depends on the extent of contamination and the degree of anisotropy and heterogeneity of the soils, among other factors. Shallow contaminated zones of limited areal extent can be treated more efficiently than large zones of contamination. A highly heterogeneous soil may have a high permeability measured in a pilot test, but most of the flow is concentrated in localized, high-permeability layers, and flow through the lower permeability matrix blocks is negligible. In this case, remediation is limited by the rate of

diffusion from the low permeability zones and may be quite slow, despite the high bulk permeability.

## **Implementation**

SVE is considered a presumptive remedy for volatile organic chemical (VOC) contamination in the vadose zone, where the flow of air can be induced at a rate sufficient to flush the gas-filled porosity in the treatment zone on, at most, a daily basis. This qualitative criterion is consistent with the limited performance data available to date. For example, based on the projects listed in Table 7-1, several hundred to hundreds of thousands of gas pore volume flushes are required to reduce contamination levels to meet risk-reduction objectives. Quantitative guidance is not yet readily available because of a lack of predictive tools. Nevertheless, despite the lack of rigorously based approaches, design and operation of SVE has been successful at many sites (Table 7-1).

Table 7-1 lists a range of SVE applications that have been implemented for various site and contaminant conditions. The volume of treated soil at SVE sites ranges from 650 cubic yards to more than 200,000 cubic yards. Chlorinated solvents and/or fuel contaminants are the most common problem, and concentrations range from low values, where probably only dissolved and sorbed phases were present, to sites where substantial NAPL contamination was present (upwards of 40 pounds of contaminants per cubic yard of soil). Reported costs vary from a few dollars per cubic yard at large sites with low levels of contamination, to more than a thousand dollars per cubic yard at sites with severe geological limitations and heavy contamination. Moreover, some of the projects were completed while others are works in progress. The information in these reports is useful for compiling evidence of the feasibility of SVE for many sites.

## **Historical Development**

SVE was developed in the early 1980s. Identifying the “first” application is controversial and was the subject of at least one patent suit in the mid-1980s. The rapid acceptance of SVE as a soil treatment technology was due in part to the relative simplicity of the governing principles (as outlined above), the early development of straightforward



**TABLE 7-1 Summary of SVE performance at field sites in the U.S. from USEPA (1996 and 1998).**

Site Name	Contaminant Type	Maximum Soil Concentration (mg/kg)	Quantity of Contaminants (lbs)	Quantity Removed (lbs)	Treatment Volume (yd <sup>3</sup> )	Soil Type(s)	Treatment Depth (ft)	Minimum Permeability (cm <sup>2</sup> )	Maximum Permeability (cm <sup>2</sup> )
Commencement Bay, South Tacoma Channel Well 12A Superfund	chlorinated aliphatics	19,000	571,000	n/a	98,200	sand, gravel	40	4.2E-07	5.4E-07
Fairchild Semi-Conductor Corporation Superfund	chlorinated aliphatics, xylenes	4,500	700,000	16,000	42,000	sand, gravel, w/silt and clay layers	60	1.8E-05	1.2E-04
Hastings Groundwater Contamination Superfund	chlorinated aliphatics	n/a	n/a	600	185,000	upper clayey silt, below fine to very fine sand	125	1.9E-10	6.2E-08
Hill AFB Site 914	jet fuel (JP-4)	10,200	200,000	211,000	5,000	sand, gravel w/clay lenses	50	4.7E-08	7.8E-08
Luke AFB North Fire Training Area	waste fuels & JP-4	1,400	n/a	12,000	n/a	silty sands, clean sands, inorganic silts	60	1.5E-08	4.5E-07
McClellan AFB Operable Unit D, Site S	chlorinated aliphatics	3,000	n/a	113,000	n/a	silty sands, fine sand, silty/clayey sand and gravel	100	1.0E-11	1.7E-08
Rocky Mountain Arsenal, Motor Pool Area	chlorinated aliphatics	n/a	n/a	70	34,000	lenses, 1-3 foot clay layer	60	1.7E-06	2.9E-05
Sacramento Army Depot Operable Unit 3 (Tank 2)	chlorinated aliphatics, waste fuel	11,000	n/a	500	650	silt	20	2.6E-11	9.3E-09

*continued*

TABLE 7-1

Summary of SVE performance at field sites in the U.S. from USEPA (1996 and 1998) (continued).

Site Name	Contaminant Type	Maximum Soil Concentration (mg/kg)	Quantity of Contaminants (lbs)	Quantity Removed (lbs)	Treatment Volume (yd <sup>3</sup> )	Soil Type(s)	Treatment Depth (ft)	Minimum Permeability (cm <sup>2</sup> )	Maximum Permeability (cm <sup>2</sup> )
Verona Well Field Superfund, Thomas Solvent Raymond Road (OU-1)	chlorinated & nonchlorinated aliphatics	n/a	16,500	45,000	26,700	fine to medium sand w/gravel and silt/clay	20	1.0E-07	2.0E-07
Camp LeJeune Military Reservation, Area A	chlorinated aliphatics, benzene	n/a	n/a	n/a	17,500	fine to medium sand w/traces of silt and clay	12	1.2E-07	2.8E-07
Davis-Monthan AFB Site ST-35	fuel	320,000	n/a	587,000	63,000	sandy clay with interbedded gravels and sands	n/a	n/a	n/a
Fort Richardson Bldg. 908 South	diesel fuel	17,000	n/a		4,600	glacial deposits	55	n/a	n/a
Holloman AFB Sites 2 & 5	fuel	17,500	n/a	44,000	9,500	clean to silty sands interbedded w/silt & clay	15	n/a	n/a
Intersil-Siemens Superfund	chlorinated aliphatics	11,000	n/a	3,000	280,000	interbedded sand and gravel with silt and clay	100	n/a	n/a
Seymour Recycling Corporation Superfund	chlorinated aliphatics	>1,000	200,000	29,000	200,000	sands, silts	6	n/a	n/a
Tyson's Dump Superfund	chlorinated aliphatics	250,000	n/a	200,000	30,000	clayey sand to silty sand	10	n/a	n/a

continued

**TABLE 7-1** Summary of SVE performance at field sites in the U.S. from USEPA (1996 and 1998) (continued).

Site Name	Maximum Design Flow (cfm)	Vertical Vents	Horizontal Vents	Offgas Treatment	Capital Cost	Annual O&M Cost	Total Cost	Status	Operating Duration (years)	Literature Reference	Est. Pore Volume Flushes
Commencement Bay, South Tacoma Channel Well 12A Superfund	3,000	22		GAC w/regeneration	\$5,314,000	\$100,000	n/a	Ongoing 1994	2.5	USEPA (1995)	14,868
Fairchild Semi-Conductor Corporation Superfund	9,000	39		GAC	\$2,100,000	\$1,350,000	n/a	Cleanup Complete	1.3	USEPA (1995)	55,480
Hastings Groundwater Contamination Superfund	860	10		GAC	\$210,000	\$160,000	\$370,000	Cleanup Complete	1.0	USEPA (1995)	905
Hill AFB Site 914	1,500	7		catalytic incinerator	\$335,000	\$132,000	\$599,000	Cleanup Complete	2.0	USEPA (1995)	116,800
Luke AFB North Fire Training Area	95	1		thermal oxidation	\$297,000	\$210,000	n/a	Cleanup Complete	1.2	USEPA (1995)	n/a
McClellan AFB Operable Unit D, Site S	2,500	17		catalytic oxidation	\$692,000	\$937,200	n/a	Ongoing 1994	1.0	USEPA (1995)	n/a
Rocky Mountain Arsenal, Motor Pool Area	340	2		GAC	n/a	n/a	\$74,600	Cleanup Complete	1.4	USEPA (1995)	2,758

*continued*

**TABLE 7-1****Summary of SVE performance at field sites in the U.S. from USEPA (1996 and 1998) (continued).**

Site Name	Maximum Design Flow (cfm)	Vertical Vents	Horizontal Vents	Offgas Treatment	Capital Cost	Annual O&M Cost	Total Cost	Status	Operating Duration (years)	Literature Reference	Est. Pore Volume Flushes
Sacramento Army Depot Operable Unit 3 (Tank 2)	365	8		GAC	\$216,000	\$808,800	n/a	Cleanup Complete	0.4	USEPA (1995)	45,547
SMS Instruments Superfund	300		2	catalytic oxidation w/acid gas scrubber	\$267,800	\$182,700	\$450,521	Cleanup Complete	2	USEPA (1995)	93,440
Verona Well Field Superfund, Thomas Solvent Raymond Road (OU-1)	1,600	23		catalytic oxidation, GAC	n/a	n/a	\$1,645,281	Cleanup Complete	4.0	USEPA (1995)	46,662
Camp LeJeune Military Reservation, Area A	500	8	1	GAC	\$222,400	\$247,500	\$469,900	Cleanup Complete	0.7	USEPA (1998)	3,708
Davis-Monthan AFB Site ST-35	123	6		burned as fuels in engines used to operate blowers	\$162,000	\$24,545	\$207,000	Ongoing 1996	1.8	USEPA (1998)	697
Fort Richardson Bldg. 908 South	220	2		none	\$116,900	\$13,530	\$252,200	Ongoing 1998	1.1	USEPA (1998)	10,086
Holloman AFB Sites 2 & 5	70	22		none	\$343,000	\$205,000	\$610,000	Closure Pending 1998	3.0	USEPA (1998)	4,303
Intersil-Siemens Superfund	38	7		GAC	\$550,000	\$41,905	\$770,000	Cleanup Complete	5.3	USEPA (1998)	139
Seymour Recycling Corporation Superfund	123		19	GAC	\$1,200,000	\$750,000	n/a	Ongoing 1996	4.0	USEPA (1998)	479
Tyson's Dump Superfund	15,000	90		GAC	\$22,000,000	\$5,350,000	\$43,400,000	Cleanup Complete	4.0	USEPA (1998)	389,333

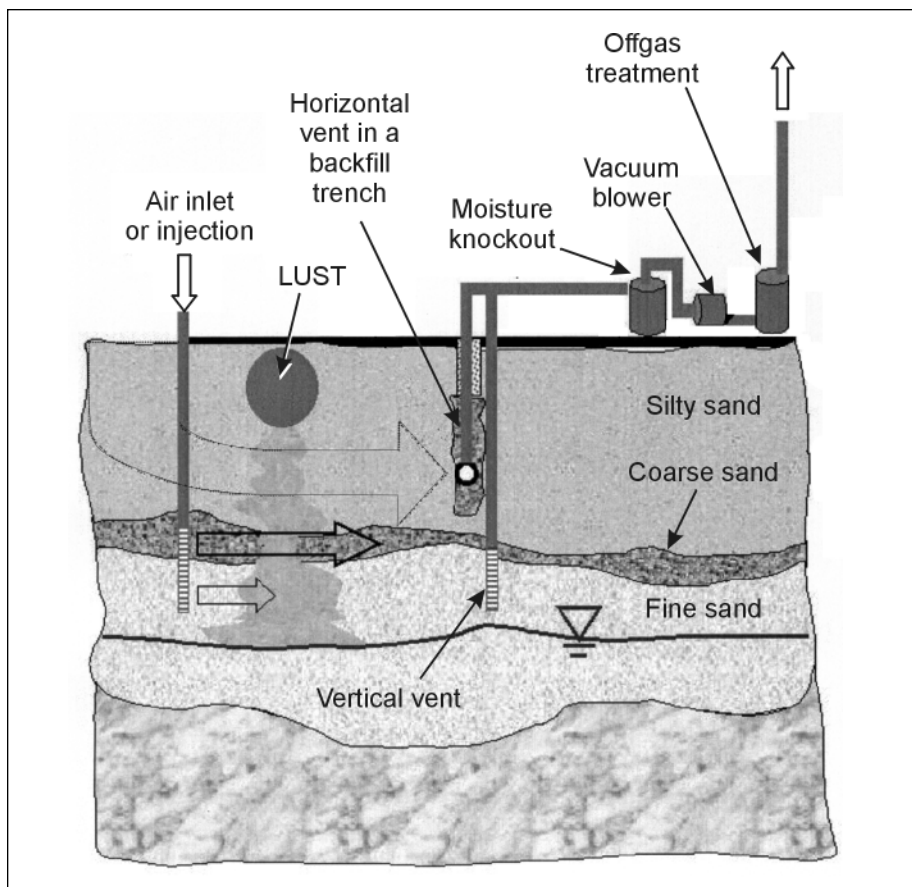
design guidance (Johnson *et al.* 1990b; U.S. EPA 1991; Michaelson 1993), and the standardization of equipment and materials (Hutzler *et al.* 1989).

SVE gained acceptance more rapidly than any other innovative treatment technology (Gierke and Powers 1997). Two factors contribute to the continued popularity of SVE: its successful remediation of many sites where effective flows are established (see more in the “Status” section below, and in U.S. EPA 1995 & 1998), and its effectiveness in reducing health risks to an acceptable level, so that treatment is no longer necessary. Demonstrations of complete removal of contaminants are few.

The basic design, installation, and operational practices have not changed substantially since those described by Johnson *et al.* (1990b), U.S. EPA (1991), Michaelson (1993), and, more recently, in a comprehensive text by Holbrook *et al.* (1998). Design refinements and new developments focus on improvements in offgas treatment, blower performance and durability, and efficiency of screens. Predictive tools for forecasting SVE performance and optimizing system design have been developed but are not yet fully proven (Jordan *et al.* 1995).

## Design Considerations

The basic design considerations for SVE are the number and placement of extraction vents, selection of blower(s) to achieve desired flow rates, and selection of the offgas treatment system (Figure 7-3). When suction is applied using a blower, air flows from the ground surface, through the contaminated zone, and to extraction vents. An impermeable barrier at the ground surface may impede the flow of atmospheric air and is sometimes used to affect air flow pattern to vents. Where the treatment area is covered or where heterogeneities/anisotropic conditions exist that limit vertical air movement, subsurface flows can be modified by either allowing air to flow into inlet vents (vents open to the atmosphere) or by injecting air or treated offgas into vents. Sparge wells, which inject air below the water table, are also sometimes used in SVE. Inlet vents are usually sufficient to prevent stagnant zones and encourage flow deep into heterogeneous/anisotropic soils. Air injection can cause contaminant vapors to move away from the treatment zone. It is



**Figure 7-3.** Conventional SVE configurations for removal of volatile contaminants from the vadose zone shown for a leaky underground storage tank (LUST) situation.

common to configure extraction vents so they can operate as either extraction or inlet vents.

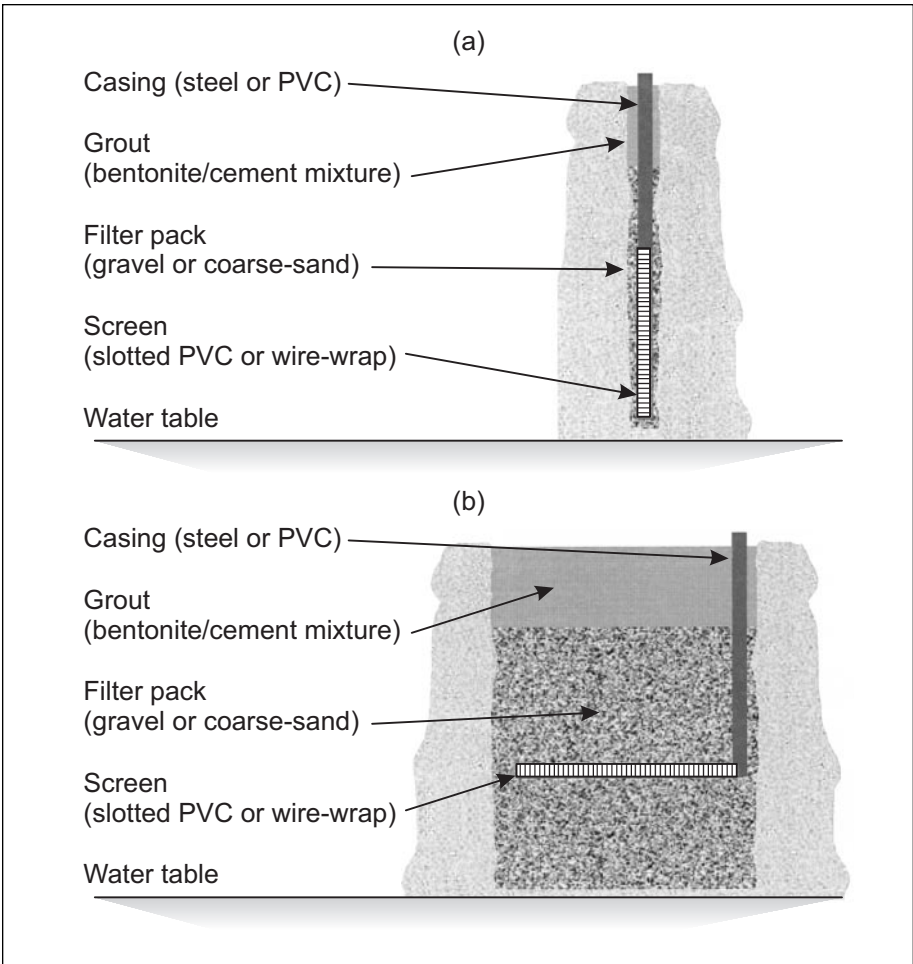
### Vents

Most SVE vents utilize water-well screens and casing that are installed vertically in the vadose zone, much like water wells in aquifers. Preferably, the screen on the vent is located below the contaminated zone (U.S. EPA 1991; Shan *et al.* 1992). In shallow settings (less than

4-m deep), installation of horizontal vents to obtain more efficient vapor flow is feasible and sometimes more practical (U.S. EPA 1991; Aiken 1992).

The number of vents is usually determined by the size of the contaminated area and the radius of influence (ROI) of the extraction vents. Vents are situated so that their ROI overlap and encompass the contaminated area (Johnson *et al.* 1990b and U.S. EPA 1991). This oversimplified approach is increasingly recognized as inappropriate because it ignores gas residence times (flushing rates) and hence the contaminant removal rates. A more appropriate approach is to define the treatment zone around an extraction vent based on a desired flushing rate, which can be determined for homogeneous conditions using analytical approaches (Shan *et al.* 1992) or for more general conditions using numerical models (Jordan *et al.* 1995). In either case, induced subsurface air flow is affected by heterogeneities, and rarely will actual flow patterns follow idealized predictions. Site capping, proper vent installation, and inlet/injection venting are useful methods for flow pattern control.

Vertical vent installations are predominantly completed in unconsolidated deposits using hollow-stem augers and either pea-gravel or coarse-sand filterpacks, as depicted in Figure 7-4a. Proper grouting near the ground surface is necessary to minimize “short-circuiting” of air through the filterpack. Direct-push technologies can be used to install vents in high-permeability, coarse-grained soils, but precautions need to be taken to ensure that screens do not become plugged with fine-grained sediments. There are no development methods to flush well screens in the unsaturated zone like those for wells in the saturated zone. Also, short-circuiting is likely when the top of the screen is near the ground surface. Horizontal vents can be installed in a back-filled trench as shown in Figure 7-4b, or with directional-drilling techniques. Directional-drilling installations are susceptible to screen-plugging unless precautions are taken to minimize screen contact with fines, or clog removal procedures are performed. Stainless steel wire-wrap screens are least susceptible to chemical attack and are more pneumatically efficient than slotted screens. High-density polyethylene and polyvinyl chloride slotted screens are more economical than stainless steel and are chemically resistant to petroleum hydrocarbons and chlorinated organics when concentrations are low. Steel and polyvinyl chloride are the two most



**Figure 7-4.** Vent configurations in Unconsolidated Deposits: (a) vertical and (b) horizontal trench.

common materials for vent casing and above-ground plumbing. Nominal diameters for screens, casing, and piping are usually between  $\frac{3}{4}$  and 4 inches.

The above-ground plumbing should include valves and ports to allow flexibility in flow configurations, flow metering (rates and pressures), and ports for concentration monitoring to optimize system performance.



Because there is no readily available design guidance for the above-ground plumbing specific for SVE, refer to a fluid mechanics handbook that includes gas flows. Pressure losses in the piping and fittings can be significant and should be considered (Peramaki 1993).

### **Blower Selection**

Blower selection is critical to power requirement minimization. In permeable soils, dynamic-displacement blowers typically are used to induce gas flow. Positive-displacement blowers, usually rotary-lobe, are used where the soil permeability is low. Dynamic-displacement blowers can provide high flows at low suctions, but blower performance diminishes rapidly as suction increases. Positive-displacement blowers operate at a constant flow rate over a wider range of suction, but their maximum flow rate is less than that of dynamic-displacement blowers.

In order to determine blower size for a full-scale operation, a pilot test measures *in situ* gas permeabilities. It is common to rent a blower for the pilot test and size the blower(s) that will be required for the full-scale remediation based on the pilot performance measurements (flows and vacuums), adjusted for the full-scale plumbing configurations. At sites where the soils are highly heterogeneous, such as glacial deposits, several pilot tests in different locations are performed to ensure that the desired flows can be achieved across the entire treatment area.

Thermally protected, intrinsically safe, explosion-proof equipment should be used. Blowers should not be throttled to control flow rates but rather plumbed to bleed in air from above-ground; however, this condition can be avoided altogether by properly selecting a blower to minimize power usage. Blowers must be protected from dust by filters and from liquid droplets by moisture separators or knockout drums, as illustrated in Figure 7-3. Systems are configured with a float switch to shut down the blower so that the moisture separator can be drained when it fills with water. The blower, moisture separator, and associated electrical controls are purchased as a complete system and configured to the site requirements. Three-phase 230/460-voltage blower motors are the most efficient and should be used if the appropriate electrical service is available.

## **Offgas Treatment**

The offgas treatment system can be the most expensive part of the remediation system. Granular activated carbon has the lowest capital cost, but it can be rapidly saturated, and is a poor choice where chemicals are recovered at high concentrations. Combustion and thermal/catalytic oxidation units are more expensive to purchase than granular, activated carbon but are cheaper to operate when offgas concentrations are high and if the contaminants are combustible and/or can be oxidized. Offgas treatment units/systems can be rented and some vendors provide pilot-scale units to be tried during permeability tests. Pilot tests tend to over-predict contaminant removal rates. Therefore offgas treatment should be considered over the long term by providing for flexibility to either adjust operating conditions when concentrations diminish or to switch to other treatment options.

## **Costs**

Extraction vent installation and the purchase of an offgas treatment system and blower(s) comprise the majority of capital costs. Operating and maintenance (O&M) costs include the costs of supplying power for the blower(s) and for operation of the offgas treatment system (such costs include fuel replenishment, replacement/regeneration of carbon, etc.). Initial site characterization, performance assessment, and monitoring costs are often close to the costs of remediation alone.

## **Augmenting Technologies**

Conventional SVE performs well at sites where the contaminants are relatively volatile and soils are relatively permeable to air. Augmenting technologies can be implemented to enhance both volatility and permeability at sites where these factors are limiting. There are four important methods for increasing the volatility of contaminants by heating soils: thermal conduction, radio-frequency, 6-phase joule, and steam injection; these technologies are described in the following pages. Soils also are heated by injecting hot air into vents, and this simple augmentation increases SVE performance. Hot air injection is a straightforward modification of conventional SVE and it is not described as a separate technology .

SVE usually performs poorly in low-permeability soils, especially those containing clays, because air flow rates are too slow to flush out contaminants. Rock and soil formations can be fractured to enhance their permeability. Pneumatic fracturing increases SVE performance in glacial drift as well as fractured shale (Murdoch *et al.* 1994; Frank and Barkley 1995), and hydraulic fracturing also enhances SVE in a variety of low-permeability formations (Murdoch *et al.* 1994). The efficacy of fractured systems for long-term complete cleanup is unknown because diffusion of contaminants from the unfractured matrix to the fractures may require a longer time than is known (Grathwohl 1998).

Deep soil mixing disrupts the soil fabric with a large auger, markedly increasing air flow rates within the mixed volume. Hot air or steam also can be injected to increase the volatility of contaminants, further increasing SVE recovery (Siegrist *et al.* 1995).

Large-scale, small-pressure disturbances associated with weather systems can cause gas flow into and out of the subsurface; this process is called “barometric pumping.” Barometric pumping is used as a long-term, low-operating-cost form of SVE for slow removal of diffusion-limited contamination through a combination of volatilization and enhanced bioremediation.

## Monitoring

SVE is monitored *in situ* by measuring pressures, obtaining gas samples from vents, or obtaining soil samples at various times during the project. It is monitored aboveground by measuring pressures, flow rates, and compositions of gases at the access ports in the process equipment. The variables typically monitored during SVE operation are listed in Table 7-2, but some of these variables are not necessarily representative of subsurface conditions. For example, subsurface gas pressures are needed during pilot tests for determining gas permeabilities; however, during full-scale operation they are not necessarily indicative of subsurface gas velocities, nor even useful for identifying areas where flow is occurring, because suction can be observed at vents even where the air is stagnant. A more effective measure of vent influence is change in concentrations of contaminants, oxygen, or tracers in soil gas.

Concentrations of contaminants are difficult to measure at sites where contaminants are present as mixtures. Typically, several constituents are

<div> <div>TABLE 7-2</div> <div>Variables monitored during SVE design activities and operation.</div> </div>			
Property	Measurement Location	Data Purpose	Operational Phase
Gas Pressure	<i>In situ</i> at vents	Establish radius of influence	Pilot test(s)
		Determine subsurface pressure gradients and flow directions	Pilot test(s) & Full-scale operation
		Quantify gas permeabilities	Pilot test(s)
	Above-ground piping	Size blower(s) Ensure operation consistent with blower capabilities	Pilot test(s) Full-scale operation
Gas Flows	Vent(s)	Control system flow	Full-scale operation
		Determine air permeability and blower performance required	Pilot test(s)
		Quantify contaminant mass removal	Pilot test(s) & Full-scale operation
Vapor Concentrations (total & contaminants of concern)	<i>In situ</i> at vents	Measure performance	Full-scale operation
	Above-ground piping	Measure performance	Pilot test(s) & Full-scale operation
	Offgas treatment discharge	Measure offgas treatment system performance & Discharge safety and permit compliance	Full-scale operation
Soil Concentration (total and contaminants of concern)	Soil Samples	Delineate contaminated area Establish treatment performance and compliance	Pre-treatment characterization
Temperature	Flow meters	Calculation of gas flow rates and concentrations corresponding to operating conditions	Pilot test(s) & Full-scale operation
Soil moisture	Soil samples	Establish initial conditions	Vent installation

selected as contaminants of concern (COC), such as benzene, toluene, ethylbenzene, and xylene (BTEX). Equivalent and comprehensive measures are also used, such as total hydrocarbons/VOCs (gasoline range organics) or total petroleum hydrocarbons (diesel range organics). Reductions in COC concentrations do not necessarily correlate to overall contaminant removal.

Flow rates and concentration measurements help to monitor system performance and can be used, potentially, to improve operations. When removals are dominated by advection but are transitioning towards diffusion-limited, rising extraction rates increase mass removal rates even though offgas concentrations may decrease as a result of a higher proportion of bypassing or reduction in gas residence times (allowing less time for equilibration). When the removal rate is diffusion-limited (Figure 7-2), increasing the extraction rate provides a negligible increase in the mass removal rate. Combustion and catalytic oxidation methods for offgas treatment benefit from high vapor concentrations, so monitoring concentrations (in terms of fuel value) from individual extraction vents can be used to optimize the performance of offgas treatment.

Comprehensive site characterization of permeability and contaminant distributions helps to locate extraction vents in the most permeable, highest-concentration areas, and maximizes extracted vapor concentrations, leading to maximum offgas treatment efficiency.

## Status

SVE is a mature technology with thousands of applications. A selection of detailed case studies (U.S. EPA 1995 & 1998) summarizes site and contaminant characteristics, system configuration and key design criteria, operational performance, capital and O&M costs, regulatory issues, lessons learned, technical contacts, and additional references.

The case studies "Modeling the Performance of a SVE Field Test," by M.E. Beshry, J.S. Gierke, and P.B. Bedient (*see page 1157*), and "Scale Dependent Mass Transfer During SVE" by C.K. Ho, describe applications of this technology in more detail (*see page 1170*).



## BAROMETRIC PUMPING: PASSIVE SOIL VAPOR EXTRACTION\*

SVE installation and equipment operation is impractical at many locations where it could benefit remediation. An inexpensive system using a renewable energy source and operating in the gas phase can fill the gap in these locations. Natural variations in atmospheric pressure, due to diurnal temperature fluctuations or weather changes associated with major fronts, can cause gases to flow to or from wells completed in the vadose zone. This process, called “barometric pumping,” induces large enough flow rates to provide meaningful remediation effects and can also be used for subsurface characterization.

Barometric pressure, an important, easily measured property of the near surface atmosphere, is the force per unit area generated by the weight of an air column extending upward 160 km to the top of the stratosphere (Hodgman 1952). It can be accurately measured using a simple pressure gauge, or *barometer*. The weight of the air column reflects the column’s air density, which varies markedly from the ground to the stratosphere. Air density is a strong function of temperature and it responds to heat radiated from land surfaces or water, or absorbed directly from solar radiation. Density also varies with changes in humidity, atmospheric chemistry, or other dynamic factors associated with weather systems. As a result, records from barometers show regular fluctuations or cycles. The daily cycle of sunlight and darkness causes temperature changes in the atmosphere to produce a diurnal cycle of barometric pressure that typically varies by less than a percent of the total average pressure. A complicated interplay of thermal and chemical effects in many areas cause even larger fluctuations in barometric pressure, typically a few percent of the total pressure, which occur every few days or weeks in response to major weather systems.

The fluctuating barometric pressure is transmitted into the subsurface to cause variations in the pressure of vadose zone gases, resulting in air flow from areas of high pressure to areas of low pressure in the subsurface, just as in the atmosphere. The pressure differences between adjacent zones in the subsurface that drive these flows are small and the flows that they produce are modest, often only detectable under special

---

\*This section was contributed by J. Rossabi.

conditions. As a result, the subsurface flow caused by barometric fluctuations, until recently, has been overlooked by an environmental community eager for quick solutions to vadose zone contamination. However, when specific subsurface zones are connected directly to the surface by a vadose zone well, pressure differences are much larger and can produce flows as large as 700 liters per minute from 10 cm-diameter wells. Barometric pumping can move significant volumes of air, it occurs regularly, and it is free.

Barometric pumping was recognized as an interesting phenomenon long before it was used for remediation. Native Americans used “blow-holes” (areas that mysteriously drew in or blew out air at different times) to forecast weather and as the focal point of rituals (Fisher 1992). Speleologists recognized that some blowholes were actually caves, and they showed that the air flow in “breathing” caves varied periodically as a result of barometric cycles, wind-driven pressures, preferential solar heating, or a combination of these processes. Hydrologists have recognized barometric effects since at least 1896, when Fairbanks described a well that intermittently released natural gas when barometric pressure decreased and drew air in when pressure increased (Science 1896). He noted that the rate of gas flow increased during periods of changing weather. An early monograph describing the release of carbonic acid from soil and its replacement with oxygen from the atmosphere also mentions this effect (Buckingham 1904). Among other important observations, Buckingham predicted that the pressure fluctuation in the subsurface would lag behind fluctuations in the atmosphere, and the lag time should increase with depth.

Several processes related to barometrically-derived subsurface flow are environmentally important. Pressure fluctuations resulting from barometric effects were observed in the subsurface during experiments at the proposed Yucca Mountain, Nevada, repository for nuclear waste (Ahlers *et al.* 1998). Gas flow accompanying the pressure fluctuations can change the subsurface moisture content, which could significantly affect the flow and transport of contaminants over long periods. Thus, barometrically induced flow could affect the performance of the nuclear waste repository. The naturally induced flow of radon gas through the vadose zone and into buildings hits closer to home. Many researchers (Owczarski *et al.* 1990; Narasimhan *et al.* 1990; Tsang and Narasimhan 1992; Garbesi *et al.* 1993; Robinson and Sextro 1995) have shown that

barometric pressure fluctuations affect the transport of radon gas into houses. Other investigators in the environmental field (Little *et al.* 1992; Massman and Farrier 1992; Pirkle *et al.* 1992; Forbes *et al.* 1993; Shan 1995; Auer *et al.* 1996; Ellerd *et al.* 1999; Rossabi 1999) examined the potential effects of barometric fluctuations on the transport of VOCs. They describe effects on shallow soil gas surveys, the transmission of the surface pressure to depth, and resultant gas transport in natural sediments with organic contamination.

Barometric pumping for remediation purposes has led to two primary applications: the injection of air to increase the oxygen content and stimulate aerobic biodegradation (Zachary 1993; Zwick *et al.* 1994), and the recovery of air and contaminated vapors (Rohay and Cameron 1992; Rossabi *et al.* 1994; Riha and Rossabi 1997; Ellerd *et al.* 1999). Both applications have counterparts, bioventing and SVE, that use mechanical pumps to move air, so the basic remedial processes employed by the applications are well known. Both passive vapor extraction and passive vapor injection can be used under the right conditions to control the migration of subsurface gas (such as landfill gas). Barometric pumping sacrifices the high flow rates achieved by pumps for the cost of operating and maintaining them. This tradeoff is attractive in circumstances where contaminants occur at low, but significant, concentrations. However, it is important to be able to estimate the potential effects of barometric pumping before it can be used for remediation.

### **Characterizing The Effect**

At the Savannah River Site in South Carolina, significant flow of contaminated air out of vadose zone wells was observed following drops in barometric pressure. The conceptual model explaining this occurrence indicates that the air flow in and out of wells is a result of the difference in pressure between the formation at the screened zone of the well and the atmosphere at the surface. Atmospheric pressure fluctuations are damped and delayed during transmittal through the subsurface. The delay and attenuation of pressure changes in the subsurface with respect to the surface pressure produces a pressure differential that drives flow through wells between the subsurface and the atmosphere.

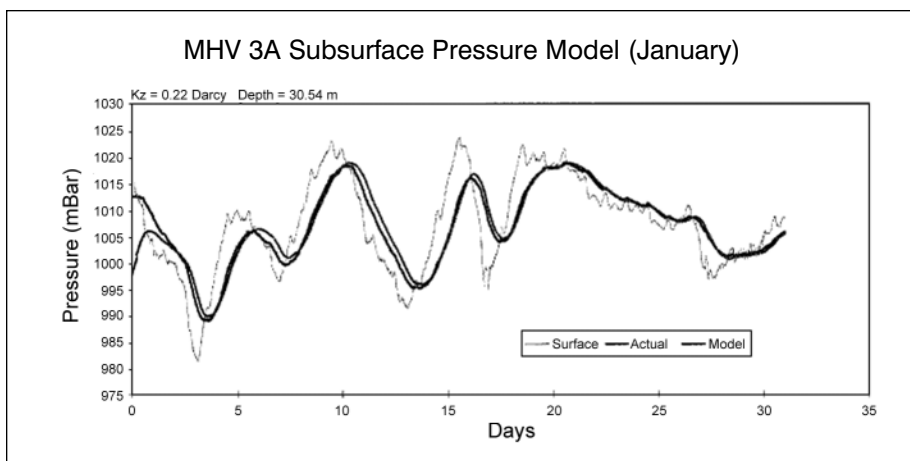
A test well was instrumented and monitored in detail to evaluate the conceptual model and to provide data to assess the effectiveness of the-



oretical predictions. The well was completed with a 2-m-long screen at a depth of 30 m in partially saturated sands and silts. Barometric pressure and the gas pressure at 30 m depth were recorded along with the gas flow rate into and out of the well during a 30-day test period in the spring of 1994.

The barometric pressure varied diurnally by a few mbar, but it varied by several tens of mbar over periods of three to five days during the test (Figure 7-5). The subsurface pressure showed little diurnal variation, but it always lagged approximately 12 hours behind the three- to five-day-long barometric fluctuations. That lag produces a pressure differential between the atmosphere and pore gases at a depth of 30 m. The pressure differential was commonly 5 mbar, with the greatest being about 12 mbar (Figure 7-5). In general, the differential was positive (atmospheric pressure is greatest, indicating that air flows into wells) when the barometer was rising, and it was negative when the barometer was falling (Figure 7-5).

Pressure differentials were sustained for approximately three to five days before changing sign. This defined periods of several days when the flow was either into or out of the well. For example, the pressure differential indicated that air was flowing out of the well on days 0-4, 6-7,



**Figure 7-5.** Barometric pressure, observed subsurface pressure, and predicted subsurface pressure in a well 30.5 m deep with a 2-m-long screen at Savannah River Site.

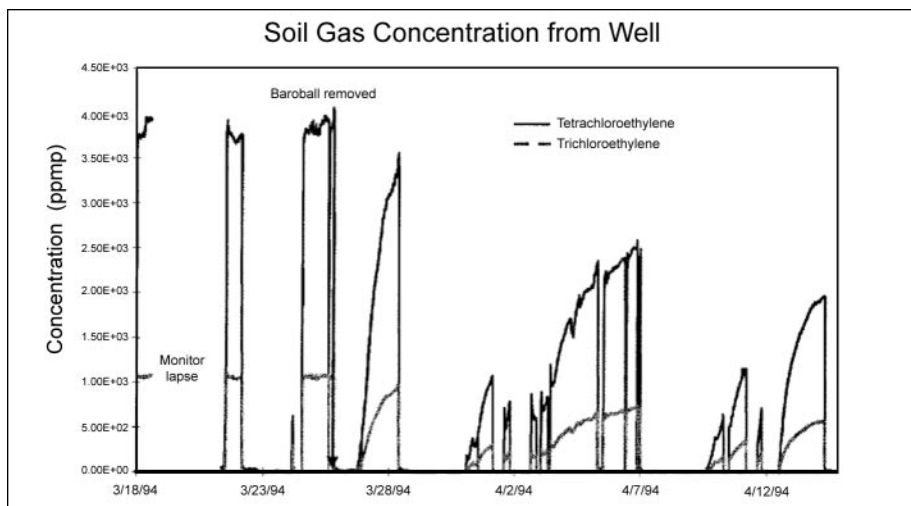
10-14, 16-17, and 21-26, whereas it flowed into the well on days 4-6, 7-10, 14-16, and 17-21. These flow periods and changes in barometric pressure corresponded to major weather systems that passed through east-central South Carolina every three to five days. Barometric pumping at this test well was driven by major weather changes, while it was largely unaffected by diurnal variations.

### **Improving Performance**

Clearly, barometric pumping can transfer substantial volumes of gas between the atmosphere and subsurface. The natural process exchanges gas equally in both directions; that is, the volume of gas that flows into a well equals the volume that flows out when averaged over several cycles. However, most applications only require transfer in one direction (injection for bioventing or recovery for passive SVE), and transfer in the other direction may actually reduce effectiveness.

At least two check valves have been developed to limit barometric pumping to unidirectional flows (U.S. Patents No. 5,641,245 and 5,697,437). The valve discussed here is a lightweight ball about 3 cm in diameter that sits in a conical seat. It functions like a common ball-type check valve with an exceptionally small cracking pressure, markedly improving the performance of barometric pumping for remediation.

During the demonstration at the Savannah River Site, a check valve prevented air from flowing into the well during the first two flow cycles, and then it was removed for the next few cycles (Figure 7-6). During the flow cycles using the check valve, concentrations of contaminants increased rapidly and were nearly constant. However, after the check valve was removed, the contaminants showed a markedly different history. They started at dilute concentrations and increased through the recovery cycle, but they never reached the concentrations that occurred during the check valve cycles, because clean air flowed into the well and diluted contaminant vapors in the subsurface. Eventually the clean air equilibrated with contaminants in the subsurface, but the gas flow cycle was faster than the contaminant equilibration process during the Savannah River Site test. Clearly, more mass is recovered when a check valve prevents unnecessary injections of air.

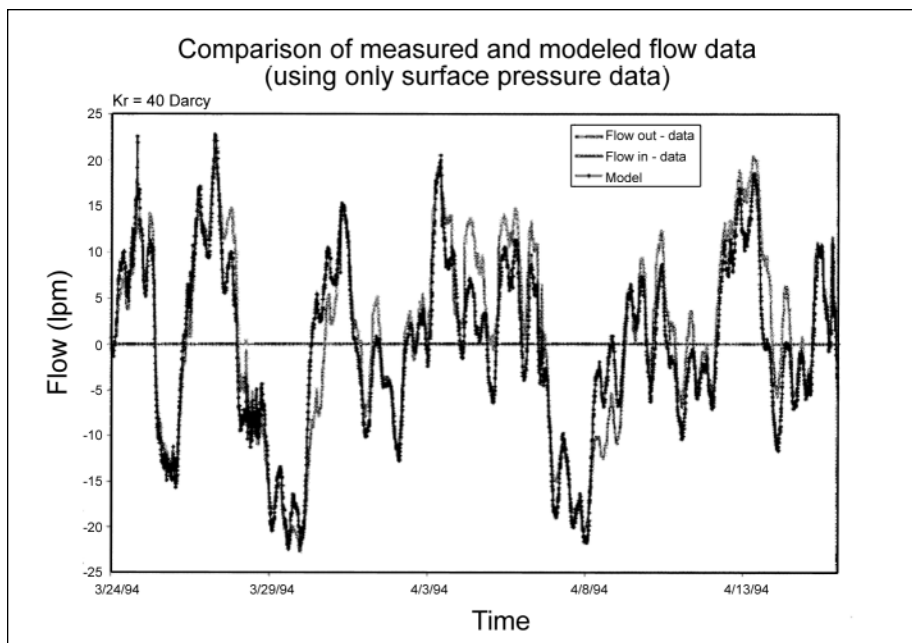


**Figure 7-6.** Concentrations of contaminants recovered from test well CPT RAM 16 by barometric pumping before and after removal of Baroball check valve.

### Predicting Performance

Theoretical models described by Weeks (1978), Shan (1995), and Rossabi (1999) played an important role in establishing the viability of barometric pumping. A simple analytical model (Rossabi 1999) using the pressure observed at the ground surface as a boundary condition precisely predicted the pressure observed during the test described above (Figure 7-5). A similar analytical model also predicts the volumetric flow rate into and out of the subsurface (Figure 7-7). Numerical models were used to predict the effects of a check valve on the flow rate and concentration at the well (Ellerd *et al.* 1999; and Rossabi 1999). All of the predictions are remarkably similar to field observations.

Those modeling efforts have shown that barometric pumping follows well-known principles, and that the effects can be readily predicted. The performance of barometric pumping can be forecast based on the characteristics of a particular site. Barometric pumping also can be adapted as a tool for site characterization; for example, by using the analysis with a parameter estimation to determine pneumatic conductivity, or using field data to determine the distribution of contaminants. These advances pave the way for useful applications of barometric pumping.



**Figure 7-7.** Volumetric flow rates as observed at test well CPT RAM 16 and as predicted using analyses described by Rossabi (1999).

## Implementation

Barometric pumping has three primary applications in the environmental field: (1) recovery of contaminants, (2) air injection to stimulate aerobic biodegradation, and (3) characterization of the subsurface. The performance of applications that recover contaminants or inject air are both improved using a check valve at the ground surface. Those applications directly parallel SVE or bioventing processes using mechanical pumps. Commonly, barometric pumping applications are labeled “passive” SVE or “passive” bioventing. Barometric pumping moves air at slower rates than mechanical pumps, so it is inappropriate for sites where remediation must be achieved quickly, or where the rate of remediation is strongly dependent on the rate of air flow through the subsurface. At many sites, the rate of contaminant mass transfer to a mobile vapor phase is relatively slow. The rate of remediation is limited by this slow rate of mass transfer, rather than by the rate of vapor flowing

through the subsurface. In such cases, the higher rates of flow that can be achieved with mechanical pumps may contribute little to the overall rate of remediation. This type of mass transfer limitation will occur at sites where SVE has already been operating for a considerable period, or where the initial concentrations are relatively low, such as at the periphery of a plume. At sites where only modest reductions in concentration are required to meet regulatory requirements, barometric pumping can successfully remediate while reducing operating costs.

Some sites are well suited to remediation by SVE or bioventing, but the economics of installing a pumping system are intractable; for example, at remote locations lacking a connection to electrical utilities, or at sites where there is not an economically viable, responsible party. Economic issues block any meaningful remedial action around the edges of many active sites, where monitoring wells penetrate contaminated ground but are not attached to an SVE system. Barometric pumping is ideal for these circumstances because it can be implemented quickly and inexpensively, and it provides a remedial process at locations that would otherwise be neglected.

The case study "Passive Soil Vapor Extraction at the SRS Miscellaneous Chemical Basin," by B. Riha and J. Rossabi, describes an application of barometric pumping at the Savannah River Site. See page 1177.



Barometric pumping is also used for subsurface characterization. Flow rates from a well and the accompanying barometric record can be used to deduce the pneumatic conductivity of the subsurface (Rossabi 1999). Moreover, chemical analyses of the vapors expelled during barometric pumping can provide insights into the amount and distribution of contaminant mass, and the rate of mass transport in vapor phase. The concentrations of vapors expelled during the first two cycles of barometric pumping shown in Figure 7-6 (check valve installed) are representative of actual subsurface conditions, whereas the concentrations during subsequent cycles (no check valve) do not accurately represent ambient subsurface conditions, because the air flowing into the well diluted the concentration of vapors. Therefore, check valves are

recommended to improve the characterization of distribution and concentration of contaminants.

Passive soil vapor injection can be used to stimulate aerobic degradation of contaminants in the subsurface by providing oxygen from the atmosphere to zones where oxygen has been depleted by chemical or biological activity. In these cases, surface air is unable to adequately penetrate the subsurface because of physical permeability limitations or because of depletion in shallower zones. A well is used to transmit air directly to subsurface zones by barometric pumping.

### **Important Factors**

Barometric pumping like SVE and bioventing is best suited to formations that are relatively permeable with relatively low moisture contents. (Like SVE, barometric pumping is hindered by sorption in extremely dry clays.)

Barometric pumping should be considered at sites where the rate of contaminant recovery is limited by the rate of mass transfer to a mobile vapor phase, rather than by the rate of air flow through the site. It also should be considered at sites that could benefit from SVE, but where the cost of installing an SVE system cannot be justified. Finally, the use of barometric pumping as an interim measure, for example, when permit or design issues delay the installation and operation of more aggressive treatment methods, is an option that is often overlooked.

Several factors uniquely affect barometric pumping performance. The process relies on a lag time between the barometric pressure and the pressure at the depth of the well screen to produce a differential that drives flow. Generally, the duration of the lag, and the magnitude of the pressure differential, increases with the depth of the well screen. As a result, the effectiveness of barometric pumping will usually increase with depth (assuming other factors are independent of depth).

Effectiveness is improved by the presence of a confining layer, such as a bed of fine-grained sediment, above the well screen. The ROI of the well increases, just as it does for a vapor extraction well, but also the rate of recovery increases by slowing the transmission of the pressure signal and increasing the pressure differential between the well and the atmosphere. Other factors, such as seasonal moisture changes or ice forma-

tion, that affect the permeability in layers between the surface and the target zone in the subsurface impact barometric pumping performance.

## Status

Barometric pumping has been used to create passive SVE systems at DOE, DoD, and private sites in the United States and abroad. Since 1990, hundreds of sites have used barometric pumping to augment more aggressive remediation systems or as standalone systems. Few careful studies of the removal effectiveness have been conducted because the chemical analysis costs are usually far greater than the system operating costs, or even the system installation costs (Riha and Rossabi 1997). At least two check valves with a small cracking pressure designed to improve the performance of barometric pumping have been patented (US Patent Nos. 5,641,245 and 5,697,437). One is commercially available under the tradename Baroball, and the other should be available soon. Published methods for designing barometric pumping applications are available largely as a result of research during implementations at DOE sites. *The Passive Voice*, an electronic newsletter edited by V. J. Rohay, was started in 1993 and continues to be an important source of information describing remedial applications for barometric pumping.

## HEATING TECHNOLOGIES

Four methods of heating the subsurface to improve remediation are currently available. All of them are intended to increase the partitioning of organic chemicals into vapor phases where they can be recovered by SVE processes. In addition, one of the heating methods, conductive heating, creates temperatures, of 500°C or higher that will oxidize contaminants in place. Six-phase resistive heating and RF heating can also create subsurface temperatures above 100°C, but they have primarily been used to heat the subsurface to the boiling temperature of water. This amount of heating will increase the rates of both degradation and recovery. Hydrous pyrolysis may oxidize organic contaminants under some conditions, and the rate of biodegradation can increase markedly with a rise in temperature.

The four heating methods draw on significantly different physical processes to transport energy into the subsurface, and, as a result, each

is particularly appropriate for certain site conditions. Thermal conduction potentially creates the hottest temperatures and is relatively insensitive to material properties, but it will only affect a small region around each heating element. Radio-frequency heating uses electromagnetic radiation that readily penetrates subsurface formations, extending the size of the region that can be heated. Steam flooding uses a hot fluid to carry heat into the subsurface. Steam follows high permeability pathways through the subsurface, however, so it preferentially heats those paths and leaves the tighter areas relatively cool. Electrical resistive heating passes an electrical current through the subsurface, heating formations where the electrical current flow is the greatest. Interestingly, electrical current flows through clays and silts more readily than through sand, so electrical resistive heating preferentially warms the clay-bearing horizons that are avoided during steam injection.

- **Effect Of Heat On Chemical Properties**—Heating improves the performance of SVE by changing the partitioning and transport properties of contaminants. For example, the following processes accompany an increase in temperature:
  - Vapor pressure of free-phase NAPL increases (Lyman et al. 1990).
  - Henry's law constant may increase due to the rise in vapor pressure, but can be constrained by smaller increases in water solubility (Davis 1997).
  - Liquid-solid sorption and vapor-solid sorption typically decrease (Ong and Lion 1991).
  - Soil moisture content decreases and very dry conditions can cause a marked increase in vapor-solid sorption (Ong *et al.* 1992)
  - Removal of soil water opens new flow paths, decreasing diffusion lengths for dead-end pore-space-trapped contaminants (Davis 1997)
  - Diffusivity in water and air increases (Lyman *et al.* 1990)
  - Volatilization of water induces steam distillation, increasing the volatilization rate of chemical species (Davis 1997)
  - Water expansion from liquid phase to vapor phase induces advection flow and mixing (Davis 1997)



- **Energy Requirements For Heating the Vadose Zone**—The four heating technologies are methods for delivering thermal energy to the subsurface, and the final temperature that is achieved will depend on the amount of heat that is delivered. The ambient temperature at a depth of 10 m is roughly 10°C in most areas. Adding thermal energy will first increase subsurface temperatures from ambient conditions to 100°C, the boiling temperature of water. Adding more heat will boil pore water and warm the surrounding region, but the maximum temperature will be maintained at 100°C until the liquid water has been removed from the vicinity of the heaters. After liquid water has been completely removed by boiling, temperatures may rise above 100°C.

The energy required to warm porous materials from ambient conditions to 100°C depends on the heat capacity. In general, the effective heat capacity is a weighted average of the heat capacities of soil solids,  $C_R$ , and water,  $C_w$ . The weighting depends on the porosity,  $\phi$ , densities of solids,  $\rho_R$ , and water,  $\rho_w$ , and the degree of water saturation,  $S_w$ . The heat required per unit volume to change the temperature of a porous material by  $\Delta T$  is

$$\Delta M_{\Delta T} = [C_R (1 - \phi) \rho_R + C_w \phi \rho_w S_w] \Delta T \quad (7.1)$$

neglecting the change of heat in the gas and non-aqueous phases. This shows that the heat required to change the temperature will depend on the degree of saturation; it will decrease as the initial saturation becomes drier. For example, consider a material with a porosity of 0.35 containing solids with a density of 2.6 gm/cm<sup>3</sup>. The heat capacity of common minerals is roughly 0.2 cal/g°C, and water is 1.0 cal/g°C. The energy required to heat that soil from ambient conditions to the boiling point of water ( $\Delta T = 90^\circ$ ) is 62 cal/cm<sup>3</sup> when the soil is initially saturated, 52 cal/cm<sup>3</sup> when the degree of saturation is 0.7, and 30 cal/cm<sup>3</sup> when the soil is initially dry ( $S_w = 0$ ).

Temperature will be maintained at 100°C while water is evaporated. The latent heat of vaporization of water,  $u_{\text{vap,water}}$ , is 540 cal/gram, and the energy required to boil all the water initially present in the soil is

$$\Delta M_{\text{vap}} = u_{\text{vap,water}} \phi \rho_w S_w \quad (7.2)$$

Boiling all the water in the soil cited above, for example, will require  $189 \text{ cal/cm}^3$  when the soil initially is saturated, and  $132 \text{ cal/cm}^3$  when the initial degree of saturation is 0.7. The energy required to boil water from soil decreases as the initial degree of saturation diminishes, but clearly, several times more energy may be required to boil all the water than to raise the temperature from ambient conditions to the boiling point.

All heating technologies must deliver thermal energy of the amounts described above to change the temperature or boil water in the subsurface. The technologies differ in the mechanism used to transfer the thermal energy through the subsurface, and these differences in the mechanism of heat transfer are the primary factor affecting their relative performances under different conditions.

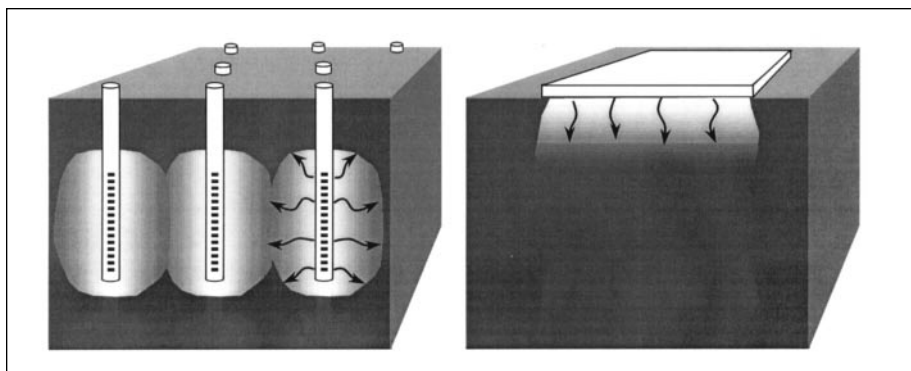
- **Soil Vapor Recovery And Treatment**—Heating increases the performance of SVE, but it can also increase the cost of the SVE operation. One factor affecting costs is related to the increase in mass of water caused by heating air. The saturated humidity of air at  $10^\circ\text{C}$  is  $10 \text{ gm of water/m}^3$ , but increasing the temperature to  $40^\circ\text{C}$  raises the saturated humidity by a factor of 5 to  $50 \text{ gm of water/m}^3$ . The increase in water content in recovered air needs to be managed by processing equipment associated with the SVE system. This typically includes equipment to condense and treat the recovered water. In addition, water may condense in cooler, low-lying areas along the SVE pipes. This can restrict vapor flow through the pipes, and the water may freeze in cold weather. Those problems can be addressed by including heat tracing or other modifications in the above ground treatment system.

### Conductive Heating\*

One of the more straightforward methods of improving SVE is to warm the subsurface by inserting rods containing electrically resistive heaters. The rods radiate heat from their outer surface and the heat is conducted through the enveloping soil (Figure 7-8). The rate of heat transfer, or heat flux, during conduction is proportional to the tempera-

---

\*This section was contributed by J. Reed and D. Conley.

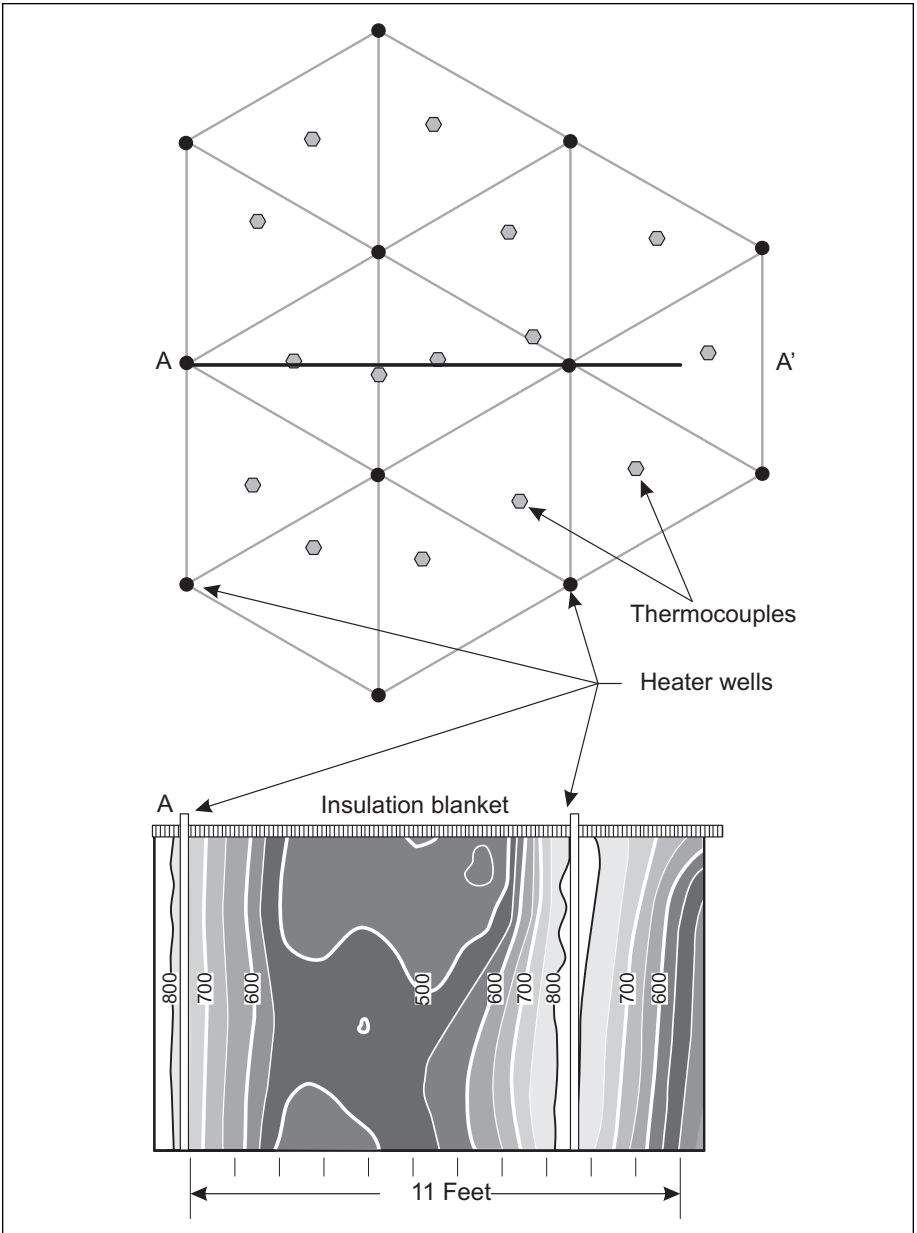


**Figure 7-8.** Thermal wells and blanket heaters used to raise subsurface temperatures by heat conduction.

ture gradient in the soil. Water near the heaters may be vaporized and the resulting steam will cause some convective heat transfer into the formation. This effect is relatively minor, however, with most heat transfer occurring by thermal conduction.

Thermal conduction from a heated rod produces a temperature profile that decreases with radial distance from the rod (Figure 7-9a). This is an inevitable consequence of the geometry of a rod-like heater, and it is analogous to the change in hydraulic head radially away from a well in an aquifer. Temperatures are greatest in the vicinity of the rod and are limited only by the thermal integrity of the heating element. As a result, this process is capable of developing extremely hot temperatures, in excess of 500°C, particularly when an array of heaters is used. Most organic compounds are destroyed in the presence of oxygen at those temperatures. The *in situ* temperature decreases with distance from the heater, however, so the zone where oxidization of organic compounds occurs is confined to within a few feet of the heater. Significant temperature increases occur beyond the zone where organic compounds can be oxidized. In this region the important remedial effect is evaporation of organic chemicals, increasing their availability for vapor extraction.

Temperatures in the vicinity of a heated rod will depend on the power of the heater, the radiant heat transfer between the rod and the soil, the thermal conductivity and heat capacity of the soil, and the spacing of neighboring heaters. The heating rate increases with thermal conductivity and decreases with heat capacity of the heated material. Both thermal conductivity and heat capacity depend on water content, but they



**Figure 7-9a.** Maximum observed temperatures in °C along a cross-section through an array of heater wells arranged in a hexagonal pattern (above). Temperature field based on measurements at thermocouples spaced every 1 to 3 ft. Data from Vinegar *et al.* (1998; fig. 5).

are relatively insensitive to grain size or mineral content. As a result, temperature changes resulting from conductive heating will be relatively independent of the type of sediment or rock being heated. Moreover, the change in temperature will be relatively uniform even in formations that are heterogeneous, such as interbedded sands and clays or fractured rock. The temperature field resulting from conductive heating depends primarily on the distance and geometry of the heat source, not on variations in geologic conditions.

Water content plays an important role in conductive heating because it changes the thermal conductivity and heat capacity of the formation. In general, as the water content decreases, the thermal conductivity diminishes much more rapidly than the heat capacity. As a result, steeper temperature gradients are required to conduct a unit of heat through a dry formation than through a saturated one. This has several important consequences during conductive heating in the subsurface. Boiling of water in the vicinity of the heater can markedly dry the formation and decrease the thermal conductivity, steepening the temperature gradient and elevating the temperature in the vicinity of the heater. Thus, drying near the heater causes temperatures to be even higher than they would otherwise be in a uniformly saturated material, which is an important asset where hot temperatures are desired to oxidize contaminants *in situ*.

Below the water table, or in large perched zones, water readily flows toward the heater if the formation is permeable, so the effects of drying in the vicinity of the heater may be negligible. Convection increases the rate of heat transfer in such cases, so the temperature increase will be smaller, but spread over a larger area compared to conductive heating in the vadose zone.

### Implementation

Thermal conduction can be implemented as a remedial technique either in the subsurface using rod-like heaters that function as thermal wells, or at the ground surface using slab heaters or thermal blankets (see Figure 7-8). Rod and slab heaters were used for remediation in approximately 10 full-scale demonstrations by TerraTherm Environmental Services. All of the examples in this section are based on the TerraTherm data. *In Situ* Thermal Desorption (ISTD), the process used by TerraTherm, is used as a trade name describing a particular implementation of thermal conduction heating (Vinegar *et al.* 1993, 1994).

Heating by thermal conduction offers two important effects that improve remediation. Like other heating methods, conduction increases SVE effectiveness by accelerating evaporation. Unlike the other methods, conduction is particularly effective at creating a zone of hot temperatures (greater than 500°C) near the heating elements. Organic contaminants can be destroyed in the presence of oxygen at those temperatures, so conduction heating can both destroy and accelerate the contaminant removal. As a result, the ISTD process is particularly robust, effectively remediating a variety of organic contaminants, which can be present initially at high concentrations. For example, ISTD has been used to remove free-phase NAPLs in the vadose or saturated zones. Perhaps even more significantly, it has also been used to effectively remediate regions containing organic contaminants with low vapor pressures, such as polychlorinated biphenyls (PCBs), which defy remediation by conventional SVE.

### **Thermal Wells**

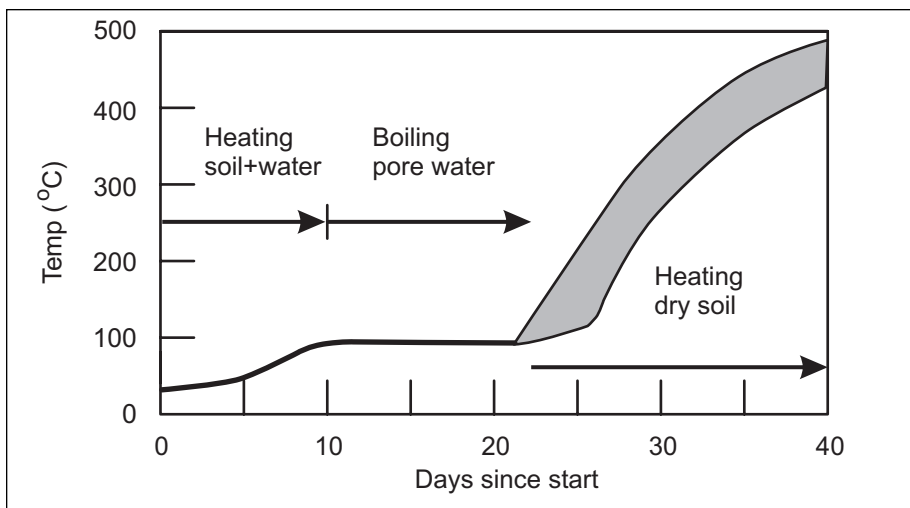
The petroleum industry developed the technology of thermal wells to increase recovery from oil reservoirs as deep as 600 m. A thermal production well contains a casing and well screen, much like a conventional SVE well, and also an electric heater. Gas and vapors are recovered by connecting the casing to a suction source, and the heater increases volatilization. Another type of thermal well contains only an electric heater in a solid casing. It is designed to heat the ground, but it lacks a well screen, so no fluids can be recovered from a heater-only well. Thermal wells are installed using conventional drilling methods, and they have been used to depths of 30 m to improve remediation (although greater depths are possible).

Thermal wells are typically arranged in a hexagonal pattern (see Figure 7-9a), with a thermal production well surrounded by a ring of six heater-only wells. The area between the wells is covered with an impermeable vapor barrier and insulating blanket. Thermal energy heats the soil, water, and contaminants, and the targeted treatment zone is maintained under suction. Vapors and gases generated by the process flow through the heated soil and are recovered at the production wells. The impermeable barrier increases the depth of air flow and inhibits fugitive emissions of contaminants.

The positions of the well screens and heaters are determined by the distribution and type of contaminant. The spacing of the wells is determined by the temperature required, the rate at which water can flow to the heated region, and other factors. Well spacings for most applications that require high temperatures are on the order of 5 to 8 ft (see, for example, Figure 7-8).

The process uses electrical heaters that can produce temperatures of 800°C or more. The thermal blankets apply 100 kW of radiant energy to the soil. Electrical heaters used in the thermal wells typically radiate several tens of kW each.

The effects of heating by conduction are illustrated by an example of the ISTD process where 12 thermal wells were used to heat PCB-contaminated ground at the Cape Girardeau site in Missouri (Vinegar *et al.* 1998). An array of 14 temperature monitoring wells with thermocouples spaced every 0.3 m with depth was used to determine heating effectiveness. The process was operated for 41 days, and there were 3 distinct periods of heating. Temperatures increased from ambient conditions to 100°C as the soil and water was heated during the first 10 days of the project (Figure 7-9b). Boiling of pore water occurred throughout the



**Figure 7-9b.** Temperature as a function of time at a depth of 2 m at the 14 thermocouple locations shown in a. Temperatures were relatively uniform prior to day 21, but they ranged over about 100° C after that time. Based on Vinegar *et al.* (1998).

region for the next 12 to 16 days, and temperatures were maintained at 100°C. The temperatures increased again between days 22 and 26, apparently because liquid water was removed completely in that time frame. Temperatures increased from 100°C to more than 400°C during the last two weeks of the project (Figure 7-9b).

### **Thermal Blankets**

Thermal blankets are slab-like heaters that are placed on the ground surface. They consist of a network of heating elements that form a panel 2.5 m by 6 m (8 by 20 ft), with a layer of high-temperature insulation 0.3 m (1 ft) thick used as backing to the heaters. The area in the vicinity of a thermal blanket is sealed with sheets of silicone rubber. Access piping within or beneath the heaters is attached to a suction source to recover vapors generated during heating.

Thermal blankets are designed to address contamination at shallow depths. While they are particularly effective at creating temperatures as high as 800°C within a few days to weeks, the treatment depth is limited to the upper 0.5 m. Organic contaminants are destroyed by pyrolysis and oxidation within the high temperature region beneath the heating elements. In addition, contaminant gases and volatile decomposition products flow upward into the high temperature region as a result of applied suction, destroying some mobile contaminants *in situ*. The remaining contaminants are collected and treated above ground.

### **Above-ground Treatment**

Process and control equipment is used to maintain temperatures in the heating modules and to collect and treat vapors from the treatment area. Process gases removed from the heated soil matrix typically contain original contaminants, oxidation products, water vapor, and atmospheric gases. These gases are treated as required using appropriate technology. For example, the risk associated with PCB releases requires that a flameless thermal oxidizer and granulated activated carbon filter be used to treat off-gases at PCB sites.

### **Monitoring And Control**

The temperature distribution in the subsurface is the single most important quantity affecting the subsurface remediation. Temperatures



are monitored using *in situ* thermocouples. The resulting data gives the temperature distribution in the treatment area (Figure 7-9a) or the temperatures as a function of time (Figure 7-9b).

### **Factors Affecting Performance**

The ISTD process is remarkably robust and it appears to be effective over a wide range of geologic conditions and contaminant properties. Nevertheless, it is by no means a technology that is suited to every case of contamination in the vadose zone. The technique is equipment- and power-intensive, and so it is relatively expensive. As a result, it is best suited to relatively small areas with high concentrations of recalcitrant compounds that defy remediation using other methods. Sites containing high concentrations of PCBs are good candidates, but a variety of other compounds have been remediated with remarkable efficiency.

The technique is particularly well suited to shallow depths where thermal blankets can be used. The cost of installing heater wells at the close spacings required to raise temperatures to several hundred °C may be prohibitive at substantial depths. The economics of this application depend on the magnitude of improvement that can be achieved and what alternatives are available, and so they should be evaluated on a site-by-site basis. This technique will be infeasible at some sites, however, where sensitive structures at the ground surface preclude the installation of either thermal wells or blankets.

The ISTD process is remarkably effective at removing organic compounds from the vadose zone. For example during one of the applications of the ISTD process, the concentration of PCBs in soil was reduced from more than 500,000 ppb to an average of 0.003 ppb (Vinegar *et al.* 1998).

### **Status**

The ISTD technology covered by U.S. Patents No. 5190405 and 5318116 has been used to treat formations contaminated with chlorinated VOCs, aliphatic and aromatic hydrocarbons (BTEX), and PCBs. The results of approximately 10 demonstrations have shown that ISTD reduces the concentration of PCBs from more than a few percent initially in a soil to less-than-detectable after treatment. Based on data from the demonstrations, ISTD was issued an interim or “draft” permit by the

U.S. EPA Office of Pollution Prevention and Toxics, as an alternative treatment for soils containing PCBs.

The status of the ISTD process has taken an important turn during the time this book has been in preparation. TerraTherm, the company that developed the process, has been dissolved and the patent rights have been transferred to the University of Texas. Licensing arrangements are currently being developed and the technology should be available from several vendors in the near future.

The case study "PCB Destruction and Removal," by John Reed and Denis Conley, describes an application of this technology. *See page 1178.*



### **Heating Using Radio Frequency Energy\***

Heating earth materials using radio frequency (RF) energy was first explored during the oil crisis of the 1970s, when tar sands were heated to recover petroleum products. This process was later refined to improve the remediation of vadose zone soils (Smith and Hinchee 1993; Davis 1997; Jarosch *et al.* 1994; Weston 1992; EPA 1995a, 1995b; Phelan *et al.* 1997).

RF heating occurs as a changing electromagnetic field interacts with molecules in the subsurface. Water is a primary target molecule, but interactions with other molecules can also be important. Water is heated in an RF field because its polar molecules rotate when the polarity of the electromagnetic field reverses. The rate at which the rotation occurs depends largely on the dipole moment of the molecule, but other factors, such as attraction to different molecules, may also be important. The dipole moment is important because optimal heating occurs when the frequency with which the electromagnetic field reverses is tuned to the rate at which the molecules can rotate. When the electromagnetic field changes polarity much faster than the molecules can rotate, then the effect of the field on the molecule is subdued. Similarly, when the change in polarity is slow compared to the rotation rate, the molecules may realign themselves and return to their original state. When the frequency of the electromagnetic field is tuned to the rotation rate, how-

---

\*This section was contributed by J. Phelan.

ever, the molecules resonate and move rapidly. Molecules other than water can also be heated by RF energy. The mechanisms will be somewhat different, but, in general, the mechanisms all produce rapid molecular motions that are manifested as an increase in temperature.

Tuning the RF transmitter to the proper frequency is important to effective heating. Microwave ovens transmit electromagnetic radiation with a frequency of 2450 MHz because water molecules are strongly influenced by this frequency. However, the depth of penetration of electromagnetic field radiation is inversely proportional to the frequency, and microwave ovens use relatively high frequencies that have limited penetration in soils. The optimum frequency range to both penetrate and interact with molecules in soils is 2 to 40 MHz, and RF transmitters that will generate this range of frequencies are typically used for soil heating.

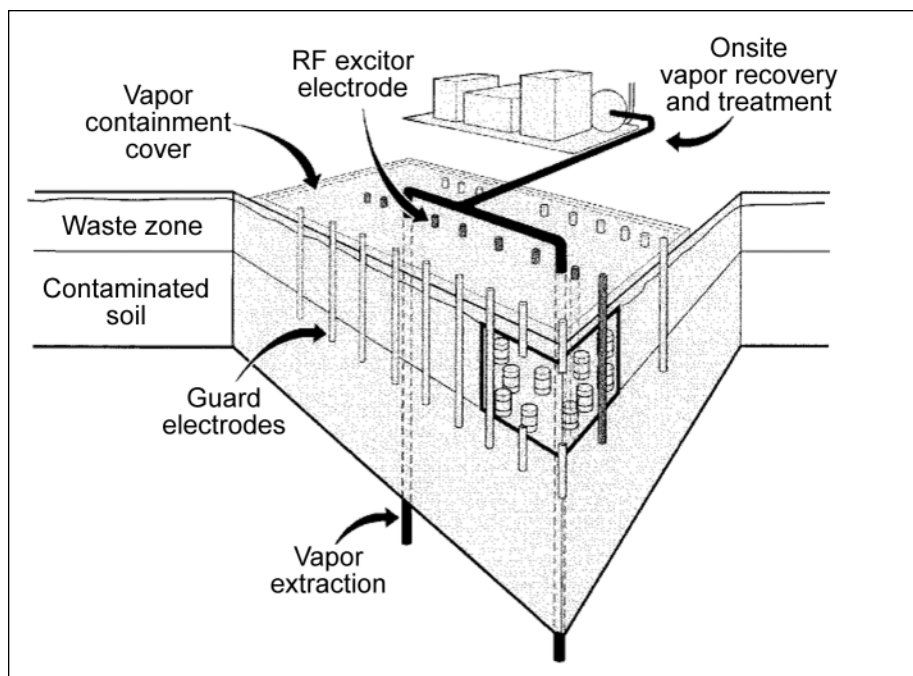
The dielectric constant of the soil is an important property affecting optimum frequency. The dielectric constant of water is 78, whereas it is between 4 and 6 for most minerals, and it is 1 for air. The bulk dielectric constant of a soil is an average value weighted to the proportions of water, minerals, air and other components (for example, contaminants) in the soil. The dielectric constant of water is much greater than the other common components of soil, so the volumetric water content is an important control of the bulk dielectric constant of soil. This means that the bulk dielectric constant will decrease as water is removed from the soil during heating. This change can be significant because it complicates the impedance matching required to optimally tune the RF transmitter to soil conditions.

Initial application of RF energy warms both soil and minerals and causes subsurface temperatures to increase to 100°C. This is followed by a period where the maximum temperatures are maintained at 100°C as pore water boils. RF heating continues to be effective after the liquid water has been removed, so the maximum temperatures may increase above 100°C. Maximum temperatures of 250°C have been achieved using RF heating, but 100°C is the design temperature for many remedial applications.

### **Field Implementation**

Two approaches have been developed for applying RF energy to soils. IIT Research Institute in Chicago, IL, uses a tri-plate array. Beginning

with a totally enclosed rectangular wave-guide, the narrow side and bottom walls are removed and the three plates are then converted into electrode arrays (Figure 7-10). The center row of electrodes is used as an exciter array and the outer row is used as guard electrodes, to reflect energy back into the central cavity. Vapor recovery occurs through one or more of the center electrodes. Electrode length and spacing depends upon the area requiring restoration. Electrode lengths demonstrated to date have been up to 8.5 m (28 ft) long with interelectrode spacing of 1.2m (4 ft) and row spacing of 3.5 m (10 ft). A single transmitter feeds all of the electrodes in the tri-plate array and is sized according to the required heating rates. An impedance-matching network between the transmitter and the electrode array is periodically adjusted as the soil heats up and soil water is removed. The exciter array electrodes are connected aboveground by the center conductor of the RF feed. A specially designed structure shields this element to keep free-field RF emissions below occupational health and communications interference criteria.



**Figure 7-10.** Tri-plate array for applying RF energy to soils.

KAI Technologies, Inc., in Woburn, MA, uses a dipole antenna. RF energy is directed through a flexible coaxial transmission line to a down-hole antenna or applicator (Figure 7-11). The dipole antenna can be from 2.5 to 15 cm (1 to 6 in) in diameter and 1.5 to 15 m (5 to 50 ft) long. The borehole must be completed with a non-metallic casing that can withstand the near-field temperatures induced by the RF energy. Vapor phase contaminant removal is performed with SVE, through the antenna borehole or an adjacent borehole. The antennae are spaced 10 to 20 feet apart to achieve uniform heating of soils in a given area. Antennas that are placed in near-surface soils must be shielded to limit radiative emissions.

### **Monitoring**

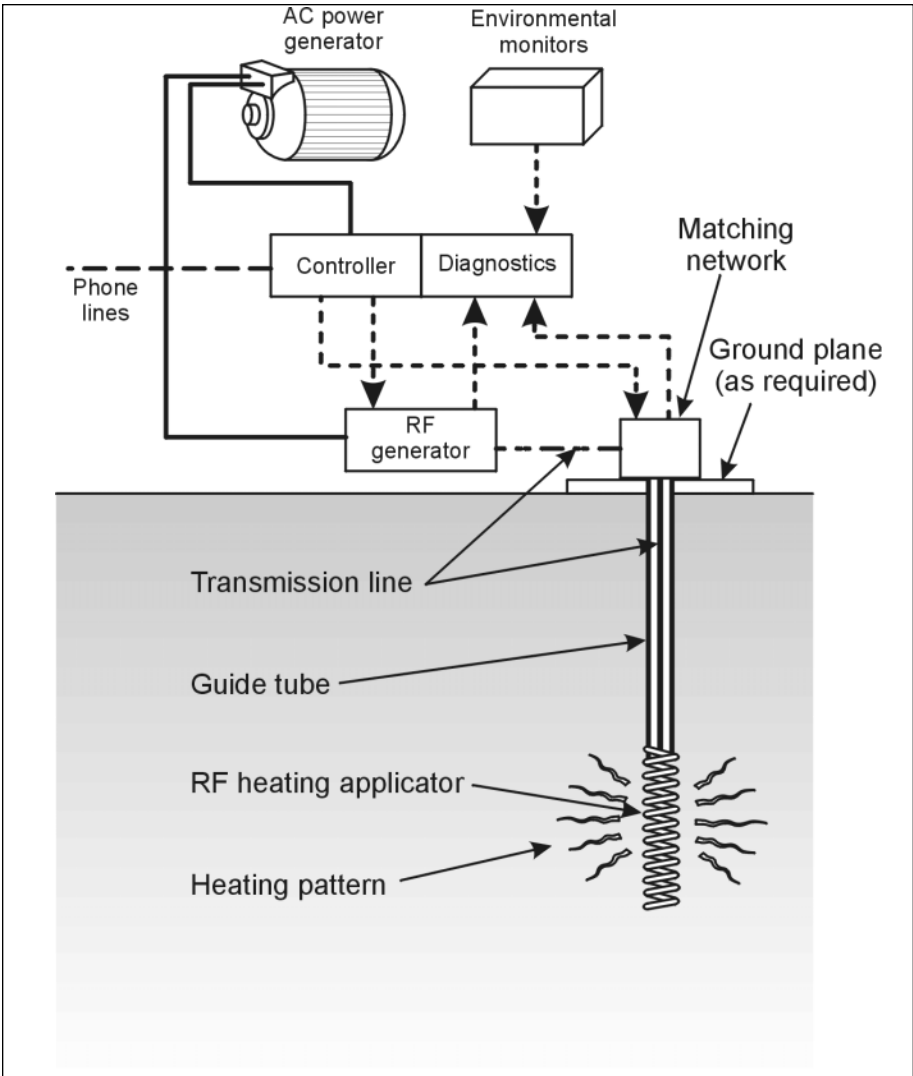
Measurement systems for RF heating include diagnostics for the RF forward and reflected power, and the impedance-matching network. Measurement of soil temperature is complicated because RF power interferes with standard temperature measurement technologies (resistance temperature devices, thermocouples, and thermistors). Temporarily turning off the RF power and making the temperature measurements with traditional technologies, or using fiber-optic-based temperature sensors while the RF energy is applied, are two options available. Moisture and contaminant monitoring are also important when evaluating system performance during operation.

### **Limiting Conditions**

Due to the bulk heating nature of RF energy, there are few instances where application of RF heating technology is not appropriate. Soil heterogeneities and moisture content variability are not significant issues since the RF energy is able to reach all areas. However, geographic areas with high precipitation rates may be problematic due to the increased energy requirements for heating and volatilization of the additional water. This will be true for all the heating technologies, however, and probably can be mitigated by covering the area to be heated.

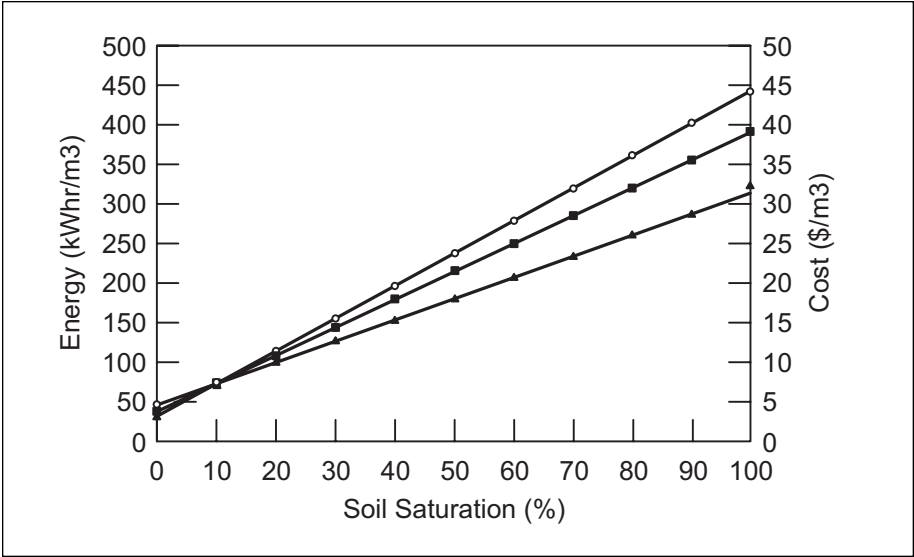
### **Economics**

The cost of RF heating will include energy costs to power the system, as well as the cost to deploy and monitor the operation. Energy costs



**Figure 7-11.** Dipole antenna for applying RF energy to soils.

depend on the soil type and degree of saturation (Figure 7-12), as well as the amount of heating required. The mass of water in soils varies significantly with the type of soil, and hence, porosity and the percent saturation of the soil pore space (Table 7-3). The amount of water in soils plays a critical part in the energy balance because it affects the bulk heat



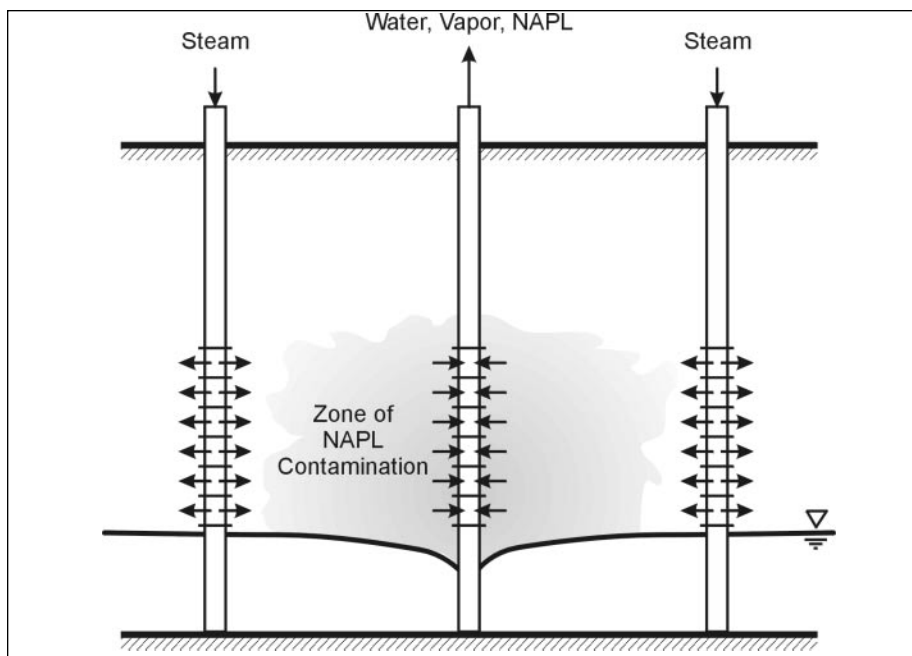
**Figure 7-12.** Energy and cost to heat and evaporate soils of variable saturation.

TABLE 7-3	Water Content of Soils (kg/m³)			
	Saturation (%)	Clay	Silt	Sand
	100	547	472	358
	90	492	425	323
	80	438	377	287
	70	383	330	251
	60	328	283	215
	50	274	236	179
	40	219	189	143
	30	164	142	108
	20	109	94	72
	10	55	47	36
0	0	0	0	

capacity (equation 7.1) and the bulk heat of vaporization. Figure 7-12 shows the energy requirements to heat one cubic meter of soil (clay, silt, and sand) to 100°C, with varying soil moisture saturation levels to the point where all soil moisture has been evaporated. Even with no soil water, about 50 kWhr/m<sup>3</sup> is needed to warm the soil from ambient temperatures to 100°C. This figure can be used to estimate the energy costs of heating to this point.

### Steam Flooding\*

Controlled steam injection can be a rapid and effective NAPL source remediation technique for many vadose zone sites. The process involves the injection of steam in one or more injection wells, with extraction of water, NAPL, and vapors from one or more extraction wells (Figure 7-13). Steam flooding can be used both with LNAPL and with DNAPL,



**Figure 7-13.** Simplified diagram of the steam injection process for remediation of NAPL source zones.

\*This section was contributed by R.W. Falta.



although issues of unwanted NAPL migration can arise at DNAPL sites. Although Figure 7-13 shows a NAPL with steam injection above the water table, steam remediation can also be performed below the water table in systems where there is strong layering or anisotropy (Newmark and Aines 1997; Newmark 1994).

Steam injection for the recovery of NAPL is a well-established practice in the petroleum industry. Steam flooding has been used for enhanced oil recovery (EOR) since the 1930s (Stoval 1934). Texts by Prats (1982), Burger *et al.* (1985), Boberg (1988), and Baibakov and Garushev (1989) are among those included in an extensive literature base on steam flooding for EOR.

Experience with steam injection for EOR projects, along with related developments in geothermal reservoir engineering, has helped promote the use of the steam injection application for environmental remediation. However, there are substantial differences between the application of steam injection for environmental purposes and for EOR applications. Vadose zone NAPL source areas are usually in shallow, unconfined systems, and are limited in scale to a few acres or less. In contrast, a typical EOR steam injection application might involve a tightly confined formation, located at a depth of a thousand feet or more, with an overall injection/extraction pattern covering tens or even hundreds of acres. In the EOR case, the oil is uniformly distributed over a large area, at high phase saturations in the range of approximately 50 percent. On the other hand, typical NAPL source zones involve much smaller quantities of NAPL at lower saturations, with a highly heterogeneous and often unknown distribution.

The goals of EOR and environmental remediation differ as well. The goal of an EOR project is to economically produce oil, and a small amount of oil left in the formation after a steam flood is inconsequential. A NAPL source zone remediation project will have a completely different objective, to remove all, or nearly all, of the NAPL from the treatment zone.

### **Physical Processes**

Steam flooding for remediation depends on the delivery of energy to a targeted zone, and on the subsequent mobilization and recovery of contaminants in that zone. The processes of energy delivery and con-

taminant removal are quite different, although they are equally important to successful remediation.

### Energy Delivery

Energy delivery can be done either through the injection of hot fluids, such as steam, hot air, or hot water, or through the direct addition of energy. Examples of direct energy addition include radio frequency heating, microwave heating, and resistive heating. These direct energy techniques can be used in conjunction with steam injection to target zones, which are not effectively heated by the steam (Newmark and Aines 1997).

The heat energy required to raise the temperature in a subsurface volume depends on the heat energy content of the volume before and after the heating, and on heat losses from the volume. The heat content consists of contributions from the soil grains or rock, and from the various fluid phases present in the porous media: gas, aqueous, and NAPL. The heat content of a unit volume of vadose zone material was given in Chapter 1 as:

$$M^h = (1 - \phi)\rho_R C_R T + \phi S_g \rho_g u_g + \phi S_w \rho_w u_w + \phi S_n \rho_n u_n \quad (7.3)$$

As shown earlier in this chapter, the amount of energy required to raise a unit volume of the treatment zone from ambient conditions to steam zone conditions is computed by subtracting the value of  $M^h$  for the ambient conditions from the value for the steam zone conditions. The energy requirement calculated above corresponds to fairly modest energy costs, on the order of a few dollars per cubic meter. In general, the cost of energy is usually not a limiting economic consideration in the design of a steam flood.

Energy delivery by hot fluids can be accomplished through the injection of steam, hot water, hot air, or some combination of the three. For a given mass injection rate, the rate of energy input is determined by the injected fluid's specific enthalpy. As discussed in Chapter 1, the specific enthalpy of fluids varies dramatically depending on whether they are liquids, condensable gases (such as steam), or noncondensable gases (such as air). For example, the specific enthalpy of liquid water at 100°C is 419 kJ/kg, while the specific enthalpy of steam at this temperature is much higher, 2676 kJ/kg (Sonntag and van Wylen 1982). The difference

is heat of vaporization, which is the energy required to evaporate a unit mass of the liquid. Steam has a very high specific enthalpy due to the high heat of vaporization of water, 2257 kJ/kg at 100°C. For this reason, a large amount of energy is used to convert liquid water into steam initially, in the boiler. This energy is released when the steam condenses at the steam front. The steam condensation at the steam front forms the basis for a very efficient heat transfer mechanism.

The steam condensation front velocity and the steam Darcy velocity in the steam zone are important features of a steam flood. The steam front velocity is the speed at which the leading edge of the steam zone advances. The steam front is characterized by an exponential decline in the temperature from the steam zone temperature, which is nearly constant (Menegus and Udell 1985; Stewart and Udell 1988; Hunt *et al.* 1988). These profiles, as well as the pressure profile and the steam front velocity, can be determined analytically for one-dimensional conditions (Menegus and Udell 1985; Stewart and Udell 1988). Typical field steam front velocities are in the range of a few meters per day, depending on the geometry and injection rates.

Behind the steam condensation front, the steam Darcy velocity is very high. From a simple mass balance, the maximum steam Darcy velocity behind the condensation front is:

$$V_s = \frac{\dot{m}_{in} X}{\rho_g} \quad (7.4)$$

where  $\dot{m}_{in}$  is the injected water mass flux (kg/m<sup>2</sup>s),  $X$  is the injected steam quality (the mass fraction of steam in  $\dot{m}_{in}$ ), and  $\rho_g$  is the steam density, about 0.6 kg/m<sup>3</sup>. The steam Darcy velocity behind the steam front is about two orders of magnitude larger than the advancing front velocity due to the change in volume that occurs as steam condenses back to liquid water. A noncondensable gas such as air would not have this property, and the magnitudes of the advancing gas front velocity and the gas velocity behind the front would be much closer.

Fingering of the injected steam may occur due to heterogeneities in the vadose zone. Interestingly, steam floods have properties that may substantially reduce this effect, especially compared to the injection of a noncondensable gas such as air. The rate of advance of a steam front is largely controlled by the rate of heating that occurs at the front. If a

small finger of steam forms, it is subject to large heat conduction losses and tends to collapse back into liquid water, stabilizing the front (Miller 1975; Stewart and Udell 1989; Lake 1989). The large pressure gradient in the steam zone compared to the pressure gradient ahead of the steam front provides additional stability to the front (Lake 1989; Udell 1994).

While the mechanisms discussed above stabilize the steam front, it is still affected by permeability heterogeneity. This behavior has been observed in two-dimensional laboratory studies by Basel (1991), and in the field tests reported by Udell and Stewart (1989) and Newmark and Aines (1997). The heat conduction mechanism discussed above also reduces this effect for small-scale heterogeneities. Thus, it is expected that mainly the larger scale heterogeneities will influence the steam front propagation (Udell 1994).

### **Contaminant Removal**

The primary means by which steam injection improves NAPL recovery from a source zone is through a greatly increased rate of evaporation in the steam zone (Stewart and Udell 1988). This occurs, in part, because of the strong increase in chemical vapor pressures with increasing temperature, and, in part, because of the high steam velocities which are generated in the steam zone. Over the temperature range of interest, about 10°C to 100°C, a chemical's vapor pressure can increase by a factor of 50 or more. For a given gas phase velocity through the NAPL zone, the rate of evaporation of a single component NAPL is a linear function of its vapor pressure. The evaporation of a multi-component NAPL such as gasoline is somewhat more complicated. The effective vapor pressure of each chemical component in a multi-component NAPL is a function of the product of the component's mole fraction in the NAPL, with its pure vapor pressure. Nonetheless, the vapor pressure of all of the components in the multi-component mixture will increase with increasing temperature. This distillation effect has been investigated by Hunt *et al.* (1988), Basel (1991), and Adenekan (1992), among others.

The high steam velocity behind the condensation front provides an efficient mechanism for NAPL evaporation. While it is obvious that contaminants with boiling points lower than the steam temperature will be removed, contaminants with higher boiling points also can be removed efficiently, as long as the NAPL evaporation front velocity is as large as

the steam condensation front velocity (Falta 1992b; Yuan and Udell 1993). Using a numerical analysis, Falta *et al.* (1992b) concluded that steam flooding would operate most efficiently for chemicals with boiling points less than about 175°C. Yuan and Udell (1993) arrived at a similar conclusion using a theoretical analysis which included the effects of mass-transfer-limited NAPL evaporation.

These theoretical results are consistent with the experiments of Basel (1991), which demonstrated efficient steam removal of xylene from a two-dimensional sand pack, and with the experiments of Stewart and Udell (1988), Basel (1991), and Yuan and Udell (1993), using mineral oil, diesel fuel, and dodecane, where the removal was much slower.

Experiments by Hunt *et al.* (1988); and Basel (1991) have shown that volatile or semi-volatile NAPL evaporated from the steam zone can condense into a high saturation NAPL bank at the steam condensation front. This concentration of the NAPL at a high saturation results in an increase in the NAPL relative permeability, making it mobile. Other features of a steam flood which help improve separate phase NAPL displacement at and ahead of a steam front include: reduction of NAPL viscosity with increased temperature; high displacing pressure gradients, due to the high steam zone velocities, and reduced capillary effects, due to lower surface tension at high temperatures.

If the NAPL in the treatment zone is an LNAPL, this mobilization is likely to be beneficial to the steam flood efficiency, and there is probably little danger in unwanted mobilization. However it may not be desirable to concentrate and mobilize a DNAPL ahead of the steam front. Since most DNAPL chemicals (for example, PCE, TCE, DCE, TCA, carbon tetrachloride, and chloroform) have boiling points below 175°C, they can be expected to form a mobile bank ahead of the steam front. Unless there is some type of confining unit below the steam zone, it is possible that the DNAPL bank ahead of the steam front might migrate downward, out of the treatment zone. The downward mobilization of NAPL can be reduced by using special steam flood designs.

The large steam Darcy velocity behind the steam front provides a powerful stripping effect for a chemical dissolved in the pore water. Due in part to the volume reduction that occurs when steam condenses back to liquid water, hundreds of pore volumes of steam are injected for each pore volume of porous media swept by the steam condensation front. This steam stripping is enhanced by the increase in the Henry's constant

that takes place when the pore water is heated to the steam temperature. The combination of these effects makes it unlikely that much dissolved chemical remains far behind the steam front unless it has a very low Henry's constant, or unless it is strongly adsorbed (at the steam temperature).

Udell (1994) shows that a large reduction of dissolved VOC concentrations can result from vaporizing the pore water in the steam zone. Boiling off only a few percent of the pore water in a steam zone (by dropping the pressure) could lead to a reduction of the aqueous VOC concentration by several orders of magnitude, due to the volume change which occurs when the liquid water vaporizes into a gas, followed by equilibration of dissolved VOC with the gas.

Other possible mechanisms for contaminant removal by steam injection include enhanced thermal desorption of adsorbed compounds (Udell 1994), dilution of dissolved nonvolatile contaminants (Vaughan *et al.* 1993), and hydrous pyrolysis/oxidation of dissolved organic compounds (Knauss *et al.* 1997; Leif *et al.* 1998). The long-term effects of steam flooding on biodegradation rates are not well known, but the results of a field test conducted at Lawrence Livermore National Laboratory showed the presence of microbial communities in all soil samples from the steam zone, including samples collected at a temperature greater than 90°C (Newmark and Aines 1997).

### **Predictive Capabilities**

The complexity of the steam flood process limits the applicability of analytical solutions to one-dimensional systems, so numerical models are typically used to model field applications. At least seven numerical steam flood simulators have been presented in the environmental literature. The codes include T2VOC (Falta *et al.* 1995; Falta *et al.* 1992a; b), M2NOTS (Adenekan *et al.* 1993), NUFT (Nitao 1993), MAGNAS (Panday *et al.* 1995; Huyakorn *et al.* 1994), COMFLOW (Unger *et al.* 1995; Forsyth and Shao 1991; Forsyth 1994a; b), MUFTE (Helmig *et al.* 1994) and STOMP (White and Oostrom 1996a, b). All of these codes are fully implicit, three-dimensional, three-phase flow simulators that can handle anisotropic, heterogeneous, porous media properties. All of the codes assume local thermal and chemical phase equilibrium, and they allow for complete phase appearance and disappearance. Several of these codes have been validated with steam flood experimental data, and

they are useful tools for steam flood design and analysis. The mathematical basis for these codes is described in Chapter 5.

### Field Studies

The first field test of steam injection for source zone remediation was performed in 1988 by Udell and Stewart (1989) at an industrial site in San Jose, CA. An industrial solvent treatment facility was located on this site beginning in 1973, and investigations begun in 1983 indicated widespread VOC contamination in the upper 20 feet of soil. These contaminants, which included xylenes, ethylbenzene, 1,2-dichlorobenzene, 1,1,1-trichloroethane, TCE, PCE, and acetone, were found at total concentrations exceeding 10,000 mg/kg in some locations. The site hydrogeology consisted of a shallow unconfined aquifer perched on continuous clay aquitard at a depth of 19 ft. The aquifer consisted of interbedded sands, silts and clays, with a 2- to 5-ft thick sand layer near the base of the aquifer. The depth to groundwater was about 17 feet, and the formation permeability was measured with a vacuum extraction test at 8.7 Darcys.

Six steam injection wells were installed in a hexagonal pattern around a central recovery well, with five-foot spacing between the injection and recovery wells. The 18-inch diameter injection wells were drilled to a depth of 19 feet, and screened over the bottom 5 feet. The recovery well was drilled to a depth of 21 feet and was screened from the bottom to the ground surface, and the ground surface around the pattern was sealed. Prior to steam injection, a 40-hour vapor extraction study was performed at a flow rate of 23 scfm. The contaminant concentrations were high, approximately 60 grams/m<sup>3</sup> of gas. The total recovery of contaminants from the vapor extraction test was estimated at 222 lbs.

Following the vapor extraction test, steam was injected for 140 hours at an average rate of 250 lb/hr, with an injection pressure of about 6 psig. The recovery well contained a submersible liquid pump at the bottom and was also used as a vapor extraction well. The steam broke through in the recovery well after 20 hours of injection. After three days of steam injection, the steam was found in the bottom 5 feet of the flood zone, but as the test progressed, the steam zone grew vertically. Following the 140-hour steam injection, the system was shut down for eight days. Finally, the system was cycled with steam and vacuum for about two

weeks. By the end of the test, the steam zone extended to the ground surface.

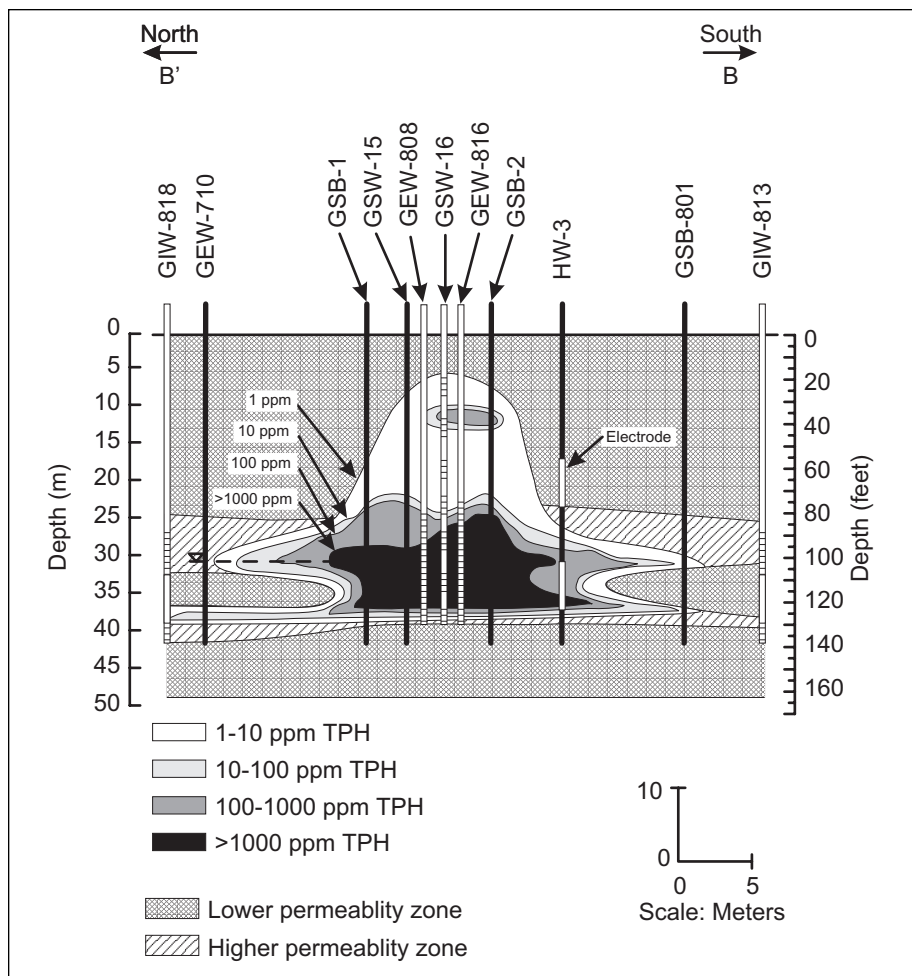
A total of 540 lbs of contaminants were removed during the steam flood part of the experiment, with about 95 percent of the recovery occurring in the vapor phase. Udell and Stewart (1989) report a reduction in total contaminants from about 1,200 mg/kg to 23 mg/kg in the high permeability parts of the treatment zone, with lower recovery in the low permeability regions.

A full-scale field demonstration of steam flooding with supplementary electrical heating was performed at the Lawrence Livermore National Laboratory, Livermore, CA, in 1993 (Newmark 1992; Newmark 1994; Udell 1994; Newmark and Aines 1997). The contaminant at this site was gasoline, which leaked into the subsurface from underground tanks. The site hydrogeology consists of alluvial deposits, with strong layering. These layers range from coarse gravels to fine silts and clays, with large variations in permeability in adjacent units. Site characterization results yielded an estimate of 6,200 gallons of gasoline, located both above and below the water table. The gasoline was found as far as 30 feet below the water table due to past water table fluctuations. Figure 7-14 from Udell (1994) is a cross section of the site showing the initial gasoline distribution. As shown in the figure, there were two continuous high permeability layers in the contaminated zone, one above and one below the water table, separated by a contaminated clay layer.

The steam treatment system consisted of six steam injection wells, and three extraction wells, as illustrated in Figure 7-15. The injection wells surrounded the contaminated zone in a rough hexagonal pattern, with the extraction wells located near the center of the zone. The spacing between the injection and extraction wells ranged from about 35 to about 90 feet. The six steam injection wells had special completions, with screened zones in the permeable layers and electrodes in the clay layer. Three electrical heating wells were also installed in the pattern, with electrodes in the clay between the high permeability zones, and above the upper high permeability zone. The recovery wells were screened across the contaminated zone. Figure 7-14 illustrates the various well completions.

The remediation operation included three phases: (1) an initial electrical heating of the clay zones and an initial steam flush, (2) a second

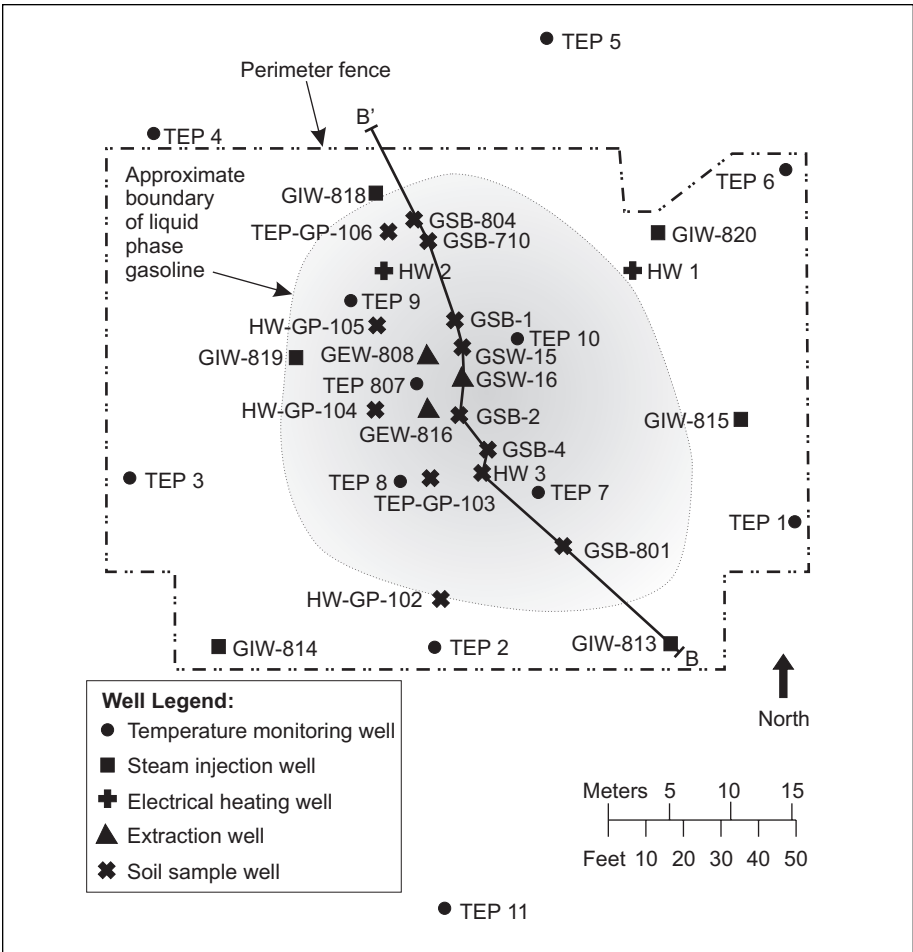




**Figure 7-14.** Cross section through the Lawrence Livermore gasoline site prior to steam flood (from Udell 1994).

steam flush, and (3) a final electrical heating and vapor and ground water extraction (Newmark and Aines 1997).

The electrical resistance heating involved a power input of up to 800 kW, with each electrode applying several hundred amps at up to 600 volts. In this operation, the clay zones are preferentially heated due to their higher electrical conductivity compared to the gravel zones. This heating was performed for a period of about two months, with a total



**Figure 7-15.** Site layout for the Lawrence Livermore steam flood demonstration (from Udell 1994).

energy input of about 202 MW-hours, heating some areas of the clay above 70°C.

The first steam injection operated for 37 days, with a steam injection rate of 11,000 kg/hour. This was generated using an 8 MW gas-fired boiler. Steam first broke through in the extraction wells after 12 days of injection. Following this initial breakthrough, the individual injection well rates were adjusted so the gasoline would continue to be driven

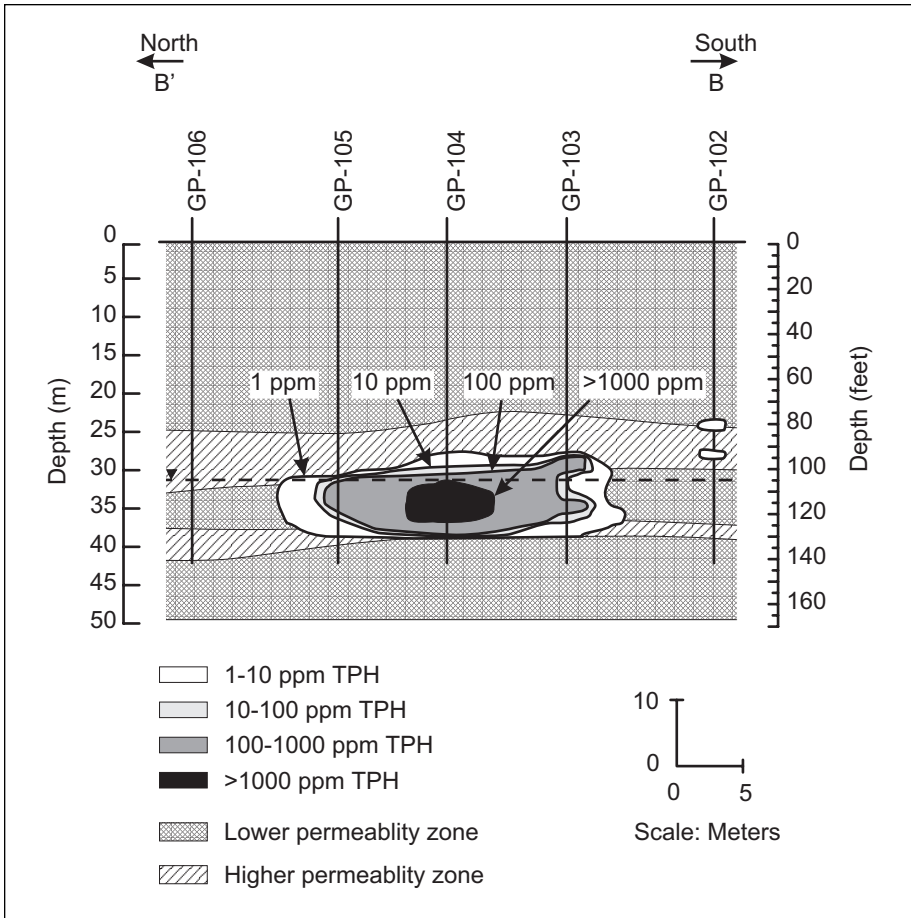
towards the center of the pattern without excessive steam losses outside the pattern. During this initial steam flood, about 1,700 gallons of gasoline were removed from the subsurface, mainly (about 85 percent) in the form of a vapor (Newmark and Aines 1997).

During the first steam flood, the gasoline vapor recovery was limited by the capacity of the treatment system. Following the first steam flood, the system was shut down for three months, and the vapor treatment system capacity was increased. The second steam flood operated for 46 days in a cyclical manner. The highest rates of gasoline vapor recovery occurred before the start of steam injection and immediately following the termination of steam injection periods, when the system was depressurized by the vapor extraction (Udell 1994). The total gasoline recovery during this phase of operations was about 5,000 gallons. Soil concentrations in the treatment zone after the second steam flood indicated that the NAPL had been removed from most of the treatment zone, except for part of the clay between the high permeability zones. This clay was cooler than the steam zone, and it was estimated that about 750 gallons of gasoline remained there. Figure 7-16 shows the distribution of gasoline after the second steam flood.

The final stage of operations involved electrical heating, groundwater extraction, and vapor extraction, without steam injection. This phase removed an additional 1,000 gallons of gasoline, for a total recovery of about 7,700 gallons. In 1995, termination of groundwater pump-and-treat and vapor extraction operations at the site were approved, and in 1996, the San Francisco Bay Region Regional Water Quality Control Board determined the remediation effort to be complete (Newmark and Aines 1997).

A field demonstration of steam flooding for chlorinated solvent removal was performed at Hill Air Force Base, Utah by Stewart *et al.* (1998). This site, known as Operable Unit 2, is located on a hillside and contains two former trenches used to dispose of spent solvents. These DNAPL liquids (trichloroethylene, Freon 113, 1,1,1-trichloroethane, and tetrachloroethylene) accumulated along a subsurface channel located on a clay layer at a depth of about 15 m below the ground surface. Prior to the demonstration, nearly 100,000 liters of DNAPL had been recovered from the site by pumping.

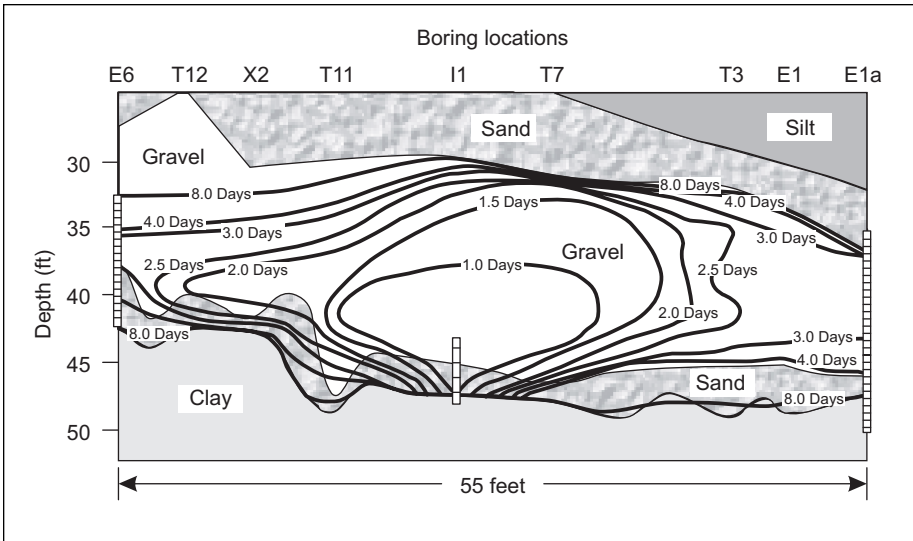
A series of extraction wells were installed along a 16.8 m segment of the subsurface channel, with a central steam injection well screened near



**Figure 7-16.** Cross-section through the Lawrence Livermore gasoline site after the second steam flush, but before final treatment (from Udell 1994).

the bottom of the channel (Figure 7-17). These wells were initially used to dewater the site, and about 5,300 liters of DNAPL were removed during this activity. Next, SVE was performed for several days. Initial SVE extraction rates were about 27 kg/hr, but these rates decreased by an order of magnitude within six days.

Steam was injected into the central well, with groundwater and vapor extraction from the outer wells. Following steam breakthrough after three days, the steam was injected at a reduced rate for eight days. A



**Figure 7-17.** Cross-section through the Hill AFB OU2 steam flood experiment (from Stewart *et al.* 1998).

DNAPL bank was produced ahead of the thermal front, and about 1,900 liters of DNAPL were produced from the test zone in the first five days of the test. Figure 7-17 shows the approximate locations of the steam condensation front during the test. The experiment concluded with 12 days of ambient air injection and SVE, along with groundwater pumping for an additional week. The total volume of DNAPL removed was 3,440 liters.

Post-test soil sampling showed 96 percent reduction of contaminant concentrations in the treated zone, and 50 percent reduction of concentrations in the underlying clay zone. Stewart *et al.* (1998) report that the cost for the demonstration was \$230 per cubic yard treated, and \$165 per gallon of DNAPL removed. They conclude that future applications could be conducted for about one-half of this cost.

The largest environmental steam flood to date is currently underway at a utility pole treating facility in Visalia, California. This full-scale application of vadose zone steam flooding is described in the accompanying case study.

"A Case Study of Steam Flooding: The Visalia Project," by R.L. Newmark, R.D. Aines, K.G. Knauss, R.N. Leif, M. Chiarappa, G.B. Hudson, C. Carrigan, J.J. Nitao, A. Thompson, J. Richards, C. Eaker, R. Weidner, and T. Sciarotta, describes a steam injection/vacuum extraction operation at Southern California Edison's Visalia Pole Yard site. See page 1181.



### Heating Using Electrical Resistance\*

Earth materials can be heated by electricity, just as an element on an electric stove is heated when an electric current flows through it. This process of *electrical resistive heating* will increase temperatures throughout a region between electrodes in the ground. Electrical resistive heating can raise the temperature of the subsurface to the boiling point of water, which creates an *in situ* source of steam to strip contaminants from the subsurface. As the contaminants are converted to vapors, they are captured and removed using standard SVE techniques. The ability to produce steam *in situ* between electrodes can produce a more uniform distribution of temperatures than steam flooding and conductive heating, where heat moves outward from wells.

Electrically, the soil and groundwater behave as a distributed matrix of resistors. As an electrical current  $I$  is passed through a soil of resistance  $R$ , the resulting power  $P$ , is  $P = I^2R$ . The heating rate is equivalent to the power dissipated in the subsurface, so heating will be greatest where the current flow is greatest. The applied voltage, rather than the current, is adjusted in the field to produce the current that is needed to induce resistive heating at whatever rate is required to accomplish timely remediation. Ohm's law states the relationship between the applied voltage and the induced current is  $V = IR$ .

The configuration of electrodes is critical to creating a uniform distribution of heat. The optimal configuration uses six metal electrodes placed in a circle around a central neutral electrode. Conversion of three-phase electricity from standard power lines into six electrical phases using standard electrical transformers powers this array. The six phases are used to energize the six metal electrodes, and the electrodes

---

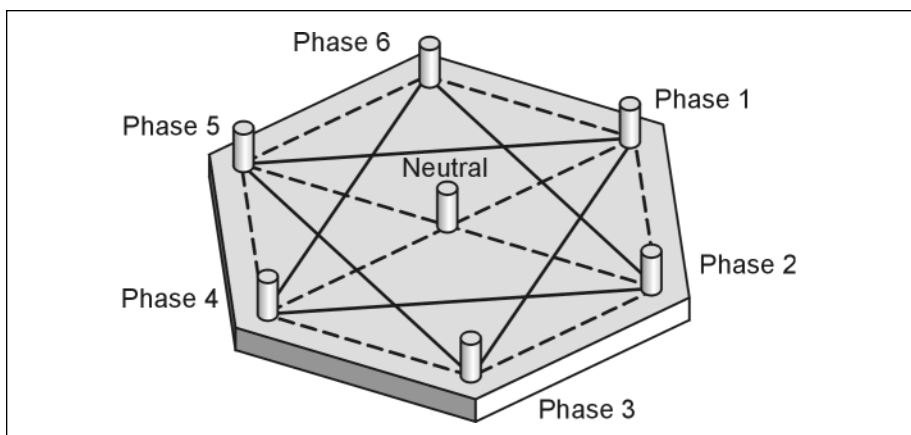
\*This section was contributed by W. Heath.

are connected in a spatially phase-sequenced pattern so that each electrode conducts to every other electrode in the formation, as shown schematically in Figure 7-18, with the central electrode acting as an electrical neutral. This electrical configuration produces a remarkably uniform heating pattern, as shown by the infrared thermal image in Figure 7-19. Figure 7-20 shows a typical field installation.

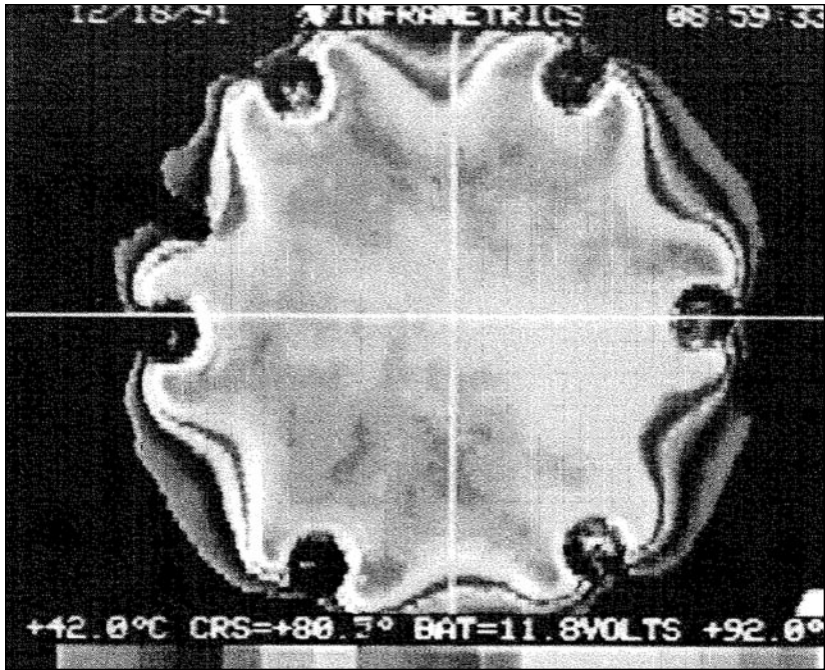
Six-phase heating appears to be an effective method to uniformly heat soil and groundwater. This technique was originally developed by Battelle Memorial Institute for the U.S. Department of Energy as a method to enhance the removal of VOCs from low-permeability soils. It is now commercially available from Current Environmental Solutions, a joint venture with Battelle Memorial Institute.

Because the soils are heated internally, low-permeability clay soils and complex heterogeneous soil formations can be effectively treated with six-phase heating.

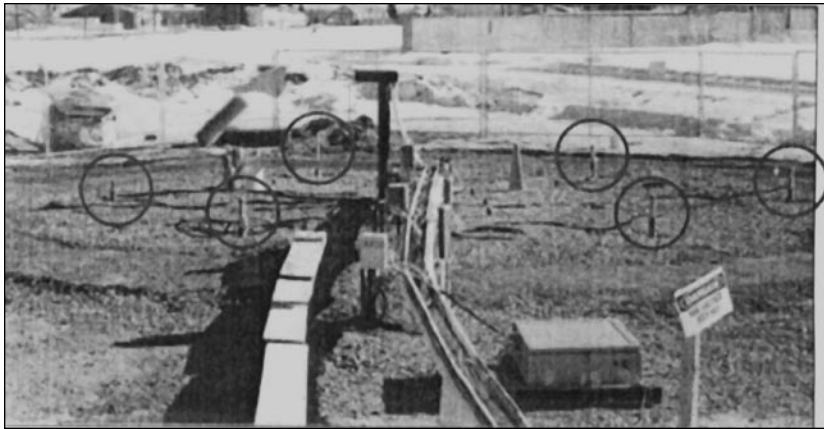
The current generated by six-phase heating concentrates within zones having higher electrical conductivity in the subsurface. The electrical conductivity depends primarily on moisture content and the concentration of free ions. As a result, low-permeability zones like silts and clays are heated preferentially because they exhibit higher moisture contents than permeable sands. This natural effect aids the treatment process by focusing heat on formations that resist advective flushing.



**Figure 7-18.** Electrode configuration and current flow paths for six-phase heating.



**Figure 7-19.** Infrared photograph of heating pattern.



**Figure 7-20.** Six-phase electrode array in a typical field installation.



For large-scale remediation efforts, multiple arrays of electrodes are operated simultaneously to treat large volumes of soil. In general, the design and placement of the six-phase heating electrodes are optimized for each site based on the following criteria:

- Size and shape of the remediation area, and total depth of site impact
- Site lithology and depth to groundwater
- Total organic carbon content and electrical resistivity of site soil
- Buried utilities and immediately adjacent surface structures

In addition to the electrodes and power supply, the major components of a six-phase heating treatment system are:

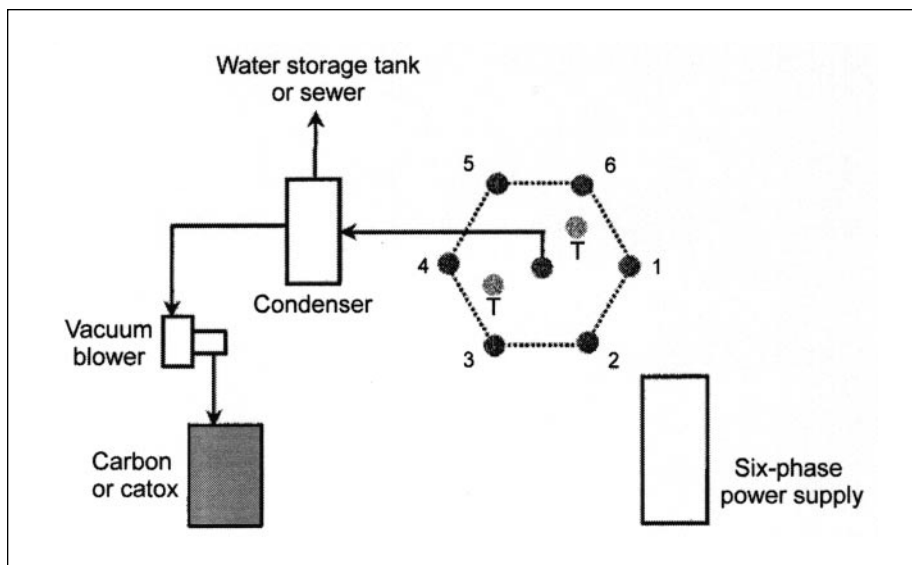
- Vapor extraction vents and monitoring wells (temperature and pressure) installed subsurface
- An off-gas collection and treatment system (including piping, a blower, a steam condenser, a condensate holding tank, and an off-gas treatment unit)
- A computer control and data acquisition system with fully remote communication

During the heating process, subsurface vapor extraction wells are used to remove steam and contaminant vapors as they are produced. A steam condenser separates the mixture of soil vapors, steam, and contaminants, which is extracted from the subsurface into condensate and contaminant-laden vapor. If these waste streams require pre-treatment before discharge, standard air abatement and water treatment technologies are utilized. Figure 7-21 shows a typical process scheme used for offgas treatment.

The case study "Vadose Zone Remediation Using Six-Phase Heating," by W. Heath describes an application of this technology. See page 1187.



The remote communication system enables complete system control (including startup, shutdown, and voltage and power adjustments) from



**Figure 7-21.** Simplified process schematic for 6-phase heating with SVE.

a remotely located computer via phone lines. The system also transmits the operational status of the six-phase heating power supplies and data from *in situ* and aboveground sensors. During system operations, the six-phase heating equipment is remotely monitored and controlled in consultation with onsite personnel.

### Case Studies

Six-phase heating technology has been deployed at the time of this writing on both pilot-scale (single electrode array) and full-scale (multiple arrays) to treat the following contaminated sites:

- Savannah River—chlorinated solvents in tight clay in vadose zone
- Dover Air Force Base—DNAPL in flowing aquifer
- Niagara Falls—groundwater heating
- Ft. Richardson—recalcitrant compound demo
- Fort Wainwright—bio/cold region demo
- Skokie Site I—full-scale DNAPL cleanup

- Cincinnati Site—LNAPL smear-zone demo
- Skokie Site II—full-scale DNAPL cleanup
- Seattle Site—full-scale groundwater cleanup

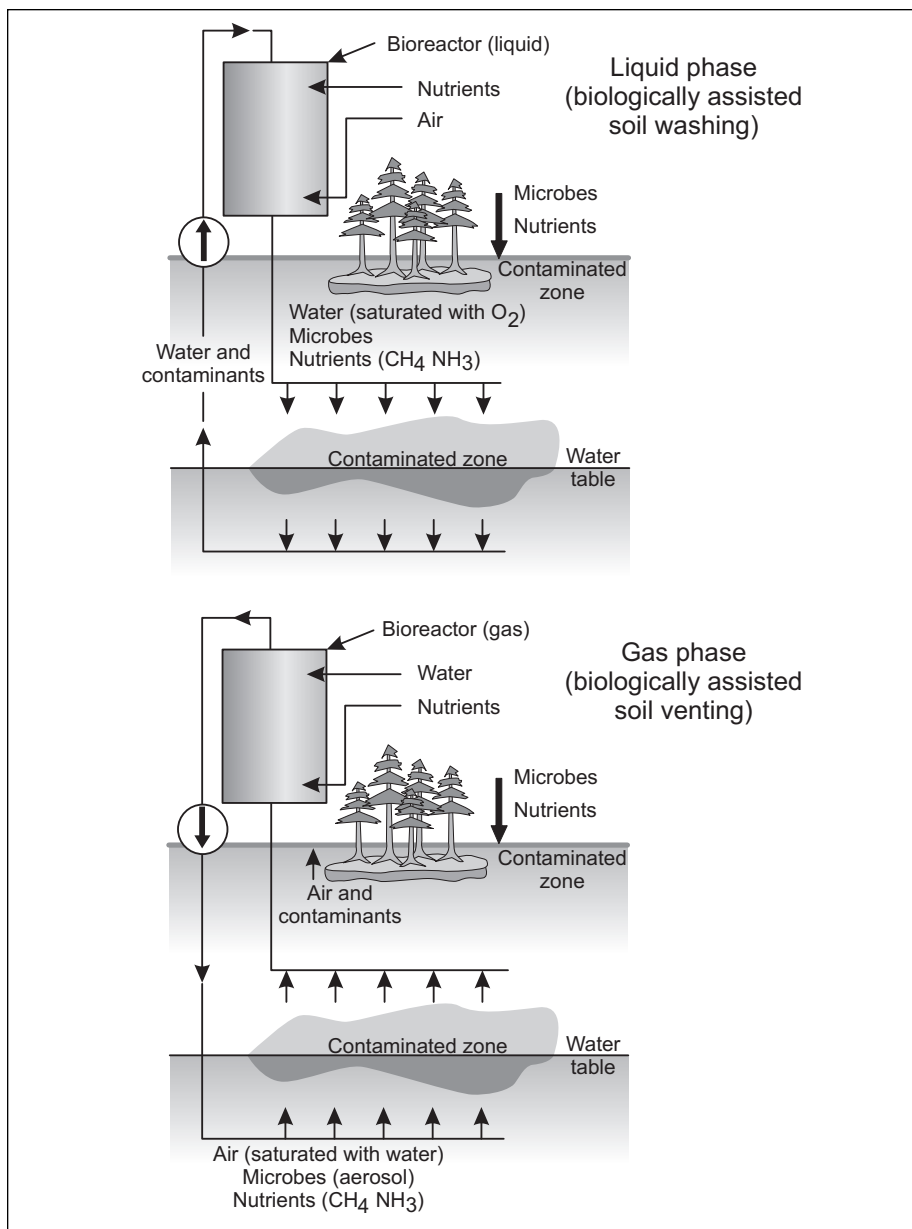
## BIOREMEDIATION\*

Contaminants can be transformed to harmless compounds during biochemical reactions orchestrated by microbes in the subsurface, and bioremediation is an engineered action that will increase the rate at which the transformation process takes place (Figure 7-22). Some organic contaminants, such as petroleum hydrocarbons, are oxidized as microbes use them as a source for carbon and energy. Other compounds, such as chlorinated solvents, are degraded by enzymes produced by microbes, even though those compounds offer no known benefit to the microbes. In other cases, metals and radionuclides can be transformed to other valence states or compounds, directly, by the microbes' use of them as electron acceptors, or indirectly, by oxidation of chelators. Both inorganic and organic compounds can be made more mobile or less mobile by stimulating production of biological surfactants or by degrading surfactants. Thus, bioremediation of contaminants can result in the complete mineralization of the contaminants, transformation to less toxic forms, immobilization, or mobilization in the vadose zone. Bioremediation is described in more detail by Hazen (1997) and McCullough *et al.* (1999). Terminology related to bioremediation is defined in Table 3.1 in Chapter 3.

Biotransformation is any alteration of the molecular or atomic structure of a compound by microorganisms. Biodegradation is the breakdown of organic substances by microorganisms into smaller organic or inorganic components. Mineralization is the complete biodegradation of a contaminant into inorganic constituents, such as carbon dioxide and water. Under anaerobic conditions, the ultimate product of biodegradation may be methane. This complete degradation of a compound is the end result of numerous biodegradation steps. These transforming and degrading processes result from the microorganisms' use of the contam-

---

\*This section was contributed by T. Hazen.



**Figure 7-22.** Both *ex situ* and *in situ* technologies use either liquid or gas to treat the vadose zone and can use horizontal wells (shown) and infiltration galleries (not shown) with strategies for biofilters, bioremediation, bioventing, biosparging, bioimmobilization, bioreactors, phytoremediation, biomobilization, biocurtin, bioaugmentation, and biostimulation.

inants as a source of nutrients or energy, changing them through various metabolic reactions. Microorganisms also can interact with contaminants and transform them from one chemical form to another by changing their oxidation state. In some cases, the solubility of the altered species increases, increasing the mobility of the contaminant and allowing it to be flushed more easily from the environment. In other cases, the opposite occurs, and the contaminant is immobilized *in situ*, thus reducing the risk to humans and the environment. Both kinds of transformations present opportunities for bioremediation of metals and radionuclides—either to lock them in place or to accelerate their removal.

Although bacteria are usually the agents in most types of bioremediation, fungi, protozoa, algae, and higher plants also can transform and degrade contaminants. Bioremediation depends on the presence of the appropriate organisms or their products in the correct amounts and combinations, and under the appropriate environmental conditions. Optimum environments for microbe growth typically consist of temperatures ranging between 15 and 45°C; pH values between 5.5 and 8.5, and nutrient ratios of 120:10:1 (carbon: nitrogen: phosphorous or C:N:P). Atmosphere and moisture also must be conducive to many types of microbial growth, and the contaminants must be close enough to the microbes, in a form that they can utilize.

Engineered bioremediation involves either adding nutrients to encourage the growth of indigenous organisms in a process called *biostimulation*, or adding specialized organisms themselves in a process called *bioaugmentation*. Both processes may be useful depending on the requirements of the site. A dozen or more specific techniques are associated with engineered bioremediation, and they are briefly described in a lexicon at the end of this section.

## Biostimulation

Biostimulation, the most common method of bioremediation in the vadose zone, requires that indigenous organisms capable of degrading contaminants already exist at the site, and that their activity can be increased to achieve a useful effect. Many contaminants, especially organic compounds, are naturally occurring or have natural analogs in the environment. As a result, indigenous organisms in most terrestrial

subsurface environments have been exposed to contaminants for extended periods of time and have adapted, or have even been naturally selected, to utilize the contaminants in their normal metabolic functions. Rarely can a terrestrial subsurface environment be found that is free from organisms that degrade or transform any compound present. Indeed, even pristine environments have bacteria that degrade contaminants. It has been shown in deep drilling studies that plasmids of bacteria living in the sediment increase as depth increases. Plasmids are exogenous pieces of DNA code for enzymes that can break down complex organics, like contaminants. Thus, as the environment becomes increasingly hostile with depth, the ability of bacteria to degrade more recalcitrant compounds increases. (Fredrickson *et al.* 1988).

Biostimulation involves first identifying the compounds that limit the activity of organisms capable of degrading contaminants, and then implementing a method for delivering those compounds to the subsurface. Water, oxygen, carbon, nitrogen, and phosphorus are essential for microbial activity, and shortages of one or more of these compounds limit biochemical degradation reactions at most sites. Not only must the compounds be present in the subsurface, but, typically, they must occur within a certain range of concentrations, and they must be in a chemical form that is available to microbes.

All significant biochemical reactions occur in the aqueous phase, so water is a key ingredient for biostimulation. Water is usually present in sufficient quantities to sustain biodegradation in most natural settings, although it must be added in some cases where previous actions, such as heating, have desiccated the subsurface.

Oxygen is often limiting since the contaminant can be used as a carbon and energy source by the organisms, and the contaminant concentration greatly exceeds the oxygen input rate from natural sources in that environment, such as diffusion from the surface. Oxygen is used as a terminal electron acceptor in respiration, allowing production of much greater amounts of energy from metabolism of organics than simple fermentation processes. Aerobic respiration is the organism's preferred mechanism of metabolism, resulting in complete scavenging of oxygen from the environment. Oxygen is commonly introduced to the vadose zone by injecting air into wells, or by tilling when contaminants are near the ground surface. Barometric pumping or wind turbines can increase air flow into the subsurface without the use of pumps. Applications in

the saturated zone use air or oxygen injected into sparge wells, or hydrogen peroxide injected into wells or distributed through infiltration galleries, a process that stimulates aerobic organisms, which are extremely effective at degrading petroleum hydrocarbons (Thomas and Ward 1992).

A C:N:P ratio of 30:5:1 is generally accepted as ideal for unrestricted growth of soil microbes (Paul and Clark 1989). However, the ratio of these compounds in pore water may differ markedly from the ideal.

Carbon can be a limiting nutrient in settings where the contaminant is a poor carbon or energy source. For example, tetrachloroethylene is a double-bonded, 2-carbon compound with 4 chlorine atoms attached. The energy required to break the double bond and cleave the chlorine atoms prevents the organism from gaining energy during degradation of this compound (Horvath 1972). A source of organic carbon other than the contaminant also is required if the total organic carbon concentration in the environment falls below 1 ppm and the contaminant clean-up levels still have not been met. As a result, fluids with a C:N:P ratio of 50:5:1 are injected for biostimulation, to slightly enrich pore fluids in carbon compared to the idealized ratio cited above (Litchfield 1993). Methane, methanol, acetate, molasses, sugars, agricultural compost, phenol, and toluene all have been added as secondary carbon supplements to the terrestrial subsurface to stimulate bioremediation (National Research Council 1993). Methane can be injected as a gas and is suited to applications in the vadose zone; the other compounds are liquids or solids and are best suited either to applications at the ground surface, such as mixing with soils by tilling, or to injection into wells in the saturated zone.

Nitrogen may be depleted where anaerobic conditions persist for extended periods of time and where the contaminant has a high carbon content. Such conditions promote denitrification and may cause nitrogen to limit the biodegradation rate. Denitrification in the saturated zone is more common than in the vadose zone. Nitrogen has been successfully introduced into the terrestrial subsurface for biostimulation by injecting ammonia, nitrate, urea, or nitrous oxide (U.S. EPA 1989).

Phosphorus is an important nutrient, but it is only required in small concentrations relative to the other nutrients. This is fortunate because phosphorus concentrations are quite low in natural waters. Phosphorus occurs most commonly in the mineral apatite, but this compound is

## Bioventing—A Simple Example of Bioremediation Design

By Brian B. Looney

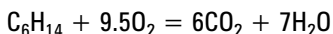
Two common bioremediation methods, bioventing and biosparging, rely on the engineered movement of air through the soil and shallow groundwater to deliver oxygen and other necessary materials. When implemented as bioventing, the method directly targets vadose zone hydrocarbon contaminants. Bioventing is closely related to soil vapor extraction and provides a good example of simple bioremediation design principles. Bioventing is distinguished from vapor extraction by incorporating modifications that maximize the role of biological destruction/detoxification (using lower airflow rates, for example). Bioventing can be implemented using either air injection or soil gas extraction, depending on site needs. Injection systems are typically less expensive and more popular because they are simpler to design and minimize offgas emission or treatment issues. This process has proven robust at a large number of sites and provides an instructive example of general bioremediation design concepts (Leeson and Hinchey 1996).

Bioventing implementation is normally customized for each site based on straightforward field tests. Also, as noted below, bioventing concepts can be modified and expanded for other classes of contaminants and other objectives (for example, cometabolism for chlorinated solvents destruction, redox manipulation for metals stabilization/detoxification, and the like.). Such modifications include innovative delivery systems, alternative reagents, and intro-

duction of alternative microorganisms. In each case, it is critical to develop a simple and consistent design concept that accounts for heterogeneity to maintain reliable performance.

*In situ* treatment methods, particularly *in situ* bioremediation, require controlled, uniform delivery of amendments to the contaminated zone. In many cases, microbial activity and contaminant destruction rate are limited by a lack of oxygen and other nutrients. In bioventing, air is injected to transport oxygen into the vadose zone.

The amount of air required to degrade hydrocarbons can be estimated by assuming a representative compound (typically hexane) is degraded according to a respiration equation:



This reaction indicates that 9.5 moles of oxygen are required to degrade 1 mole of hexane. This stoichiometric relationship is combined with soil properties and subsurface conditions to estimate rates of contaminant destruction and oxygen utilization. Details of these calculations are given in EPA (1995a) and EPA (1995b).

The degradation reaction cited above identifies a molar ratio between the utilization of carbon and oxygen. As a result, the rate at which oxygen is depleted from soil gases immediately after a bioventing system is shut down can provide a measure of performance. This type of "field respirometry" test

*continued*



provides an integrated measure of hydrocarbon destruction in the vadose zone (in units of mg of hexane equivalent hydrocarbon per kg of soil per day) according to

$$\text{Hydrocarbon destruction rate} = k_B = (0.68) (\text{oxygen depletion rate})$$

where oxygen depletion rate is measured in units of % O<sub>2</sub> per day

The equation was derived using typical values for porosity, moisture content, bulk density, oxygen density, and the like. Extreme conditions can be evaluated using the full equation presented in EPA (1995b).

Bioventing and bioparging have been used successfully under a wide range of conditions. Typical system designs generally fall into the following ranges, but there are no theoretical limits on system size:

- Typical site size = 1000 to 6000 m<sup>2</sup> (0.25 to 1.5 acres)
- Air injected into vadose zone using blower/compressor (1 to 10 hp)
- Typical total air flow = 0.6 to 2.8 m<sup>3</sup>/min (20 to 100 scfm)
- Typical radius of influence for each well = 6 to 23 m (20 to 75 feet)

System performance and the ability to reach closure criteria are commonly enhanced by increasing the density of wells to overcome mass transfer and heterogeneity limitations. Traditional bioventing relies on the interaction of microorganisms, oxygen (electron acceptor), moisture, nutrients, and aerobically degradable contaminants (electron

donor). Each of these conditions must be present, or supplied, for successful cleanup. A phased implementation normally is used to ensure viability and efficient use of resources. The typical phases are:

1. Assessment of biodegradation potential (are organisms present and active)
2. Assessment of air flow and *in situ* respiration rates
3. System design
4. Full scale operation
5. System monitoring and verification

Many sites can be remediated by bioventing alone, but the presence of recalcitrant compounds (such as chlorinated solvents), nutrient limitations, or other chemical conditions may inhibit the effectiveness of bioventing. Recent research has shown that the addition of alternate carbon sources, redox modifiers, or macronutrients may be able to overcome some site-specific limitations. One example developed by the DOE is the addition of gas-phase phosphorus to overcome limitations caused by the scarcity of this nutrient. This example is described in more detail below to show how general design concepts can be adapted to implement "new" technologies.

While bioventing design has traditionally been related to respiration stoichiometry, characterization of the hydrocarbon utilization by the biological community can be expanded to include an equation for microbial growth. The

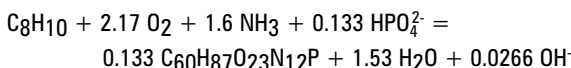
*continued*

equations below show the biomass formation stoichiometry for a representative contaminant (in this case ethylbenzene). Maximum contaminant degradation rates are generated when biomass is increased and overall site respiration rates are concurrently

increased. The equation for biomass presented below includes all of the primary macronutrients represented in cell mass. The equation is expanded to facilitate discussion of technology limitations and development potential.

### Biomass Formation (Growth)

hydrocarbon + oxygen + nitrogen + phosphorus = biomass + water + other products



It is clear that oxygen is the primary element limiting both respiration and microbial growth during aerobic biodegradation. Microbial growth rates at hydrocarbon-rich sites can be further limited by nitrogen (N) and phosphorus (P). Bioventing and biosparging provide both oxygen and nitrogen (via fixation) as air moves through the soil and shallow groundwater. This leaves phosphorus as a rate-limiting nutrient at some bioventing sites. Phosphorus can be injected into the vadose zone as an aqueous fertilizer solution; however, liquid injection increases costs and complexity and has not reliably increased performance (EPA 1995a and 1995b). Liquids injected into the vadose zone decrease the gas-phase permeability and tend to affect relatively small areas near the injection locations, whereas the

bioventing process is a large-scale volumetric process that occurs throughout the contaminated vadose zone with minimal impacts of typical levels of heterogeneity.

To overcome these limitations, scientists working for DOE developed a process that exploits the vapor pressure of alkyl phosphate esters to deliver phosphate as a component of the injected air. This process provides process control and accelerated cleanup (by increasing biomass) for bioventing and biosparging applications where phosphorus is a limiting nutrient. As with many new environmental technologies, this example shows that scientific advances are generally made in a disciplined fashion in which the baseline is improved in a step-wise manner.

nearly insoluble and effectively eliminates the bioavailability of the phosphorus it contains. Several inorganic and organic forms of soluble phosphate have been successfully used for biostimulation where phosphorus is a limiting nutrient (U.S. EPA 1989).

Even plants, such as poplar trees, have been used to biostimulate remediation of subsurface environments (Schnoor *et al.* 1995). In this case, the plants act as solar-powered nutrient pumps stimulating rhizosphere microbes to degrade contaminants (Anderson *et al.* 1993).

Biostimulation can be measured and monitored in the vadose zone using a number of direct and indirect techniques, including measurement of degradation products, like daughter products and carbon dioxide, or changes in degrading organism density. See Chapter 3 for discussion of techniques that can be used.

### Bioaugmentation

Bioaugmentation is used where indigenous microbes suitable for degrading contaminants are absent, or where non-indigenous microbes are particularly well-suited to degrading a contaminant under conditions that can be established at the site (Hazen, 1997). This approach may be particularly well-suited where:

1. Contaminants were released recently and the indigenous bacteria have not had time to adapt to the contaminant
2. Contaminants are particularly recalcitrant so that only a limited number of organisms are capable of transforming or degrading them
3. Harsh environmental conditions inhibit the establishment and maintenance of a critical biomass
4. The project objective is to cause growth that will plug the pores of a formation for contaminant containment
5. The environment can be carefully controlled, as in bioreactors, prepared beds, composting, bioslurry reactors, and land farming, so that specific inocula of high rate degraders is effective.

Novel organisms injected into the subsurface have successfully enhanced the *in situ* bioremediation of compounds that are recalcitrant

to degradation by indigenous organisms such as PCBs, chlorinated solvents, polycyclic aromatic hydrocarbons (PAHs), and creosote (National Research Council 1993). Surface applications of bioaugmentation for petroleum contaminants in prepared beds and land farming are routine since they help jump-start the bioremediation process. For controlled and carefully optimized environments, such as bioreactors, biofilters, biopiles, and bioslurry reactors, bioaugmentation is ideal, since it is relatively easy to control conditions that maximize rates of biochemical transformation or degradation.

Bioaugmentation may cause rapid growth that clogs pores and restricts additional fluid flow. This is certainly a problem where it occurs mistakenly, but it can be an important method for rapidly creating a barrier that contains contaminants. The oil industry has used bioaugmentation to plug certain zones in order to enhance oil recovery (Cusack *et al.* 1992), and similar processes have been applied to improve containment of contaminant plumes.

The relative merits of bioaugmentation and biostimulation can become blurred when the details of the processes are scrutinized. Microorganisms are commonly present in the nutrients used for biostimulation, particularly when the nutrients are in liquid form, and those organisms may augment indigenous populations when they are injected. Likewise, dead organisms are an excellent source of nutrients for most indigenous organisms. Specialized organisms injected for bioaugmentation may quickly die only to provide nutrients for indigenous organisms, which degrade contaminants. As a result, it is nearly impossible to determine if the augmentation of organisms provides a significant advantage over nutrient stimulation alone. Even some of the best controlled bioaugmentation field studies, such as caisson studies of PCB biodegradation in Hudson River sediment, failed to show that bioaugmentation was superior to biostimulation alone (Harkness *et al.* 1993).

Due to the high cost of organism production, and the lack of proof of its effectiveness, bioaugmentation probably is limited to applications where exceptional improvements are possible. For example, this is the case with genetically engineered microorganisms. It is possible that a genetically engineered microorganism could be constructed with unique combinations of enzymes to facilitate a sequential biotransformation or biodegradation of a contaminant. This would be particularly helpful for contaminants that are extremely recalcitrant, such as PCBs, or for con-

taminants that can now only be degraded under restricted conditions, such as tetrachloroethylene and carbon tetrachloride. In addition, genetically engineered microorganisms could be modified to have unique survival or adherence properties, making them better suited to the environment where they are used. Genetic engineering has been used to create microbes that will emit light when degrading contaminants, so that the rate of *in situ* biodegradation can be measured using fiber optic probes (Ripp *et al.* 1999). The effectiveness of genetically engineered, light-emitting microbes to signal the biodegradation of naphthalene was proven during field studies in large lysimeters at a DOE site (Ripp *et al.* 1999). Permitting was once thought to be prohibitive to the release of genetically engineered microorganisms, but experience and many agricultural examples have eased these concerns, and regulators in many states are willing to consider these options.

### Factors Affecting Performance

The major factors affecting the performance of bioremediation in the vadose zone include the following:

1. Site Evaluation—Ambient biochemical processes and other subsurface conditions, such as contaminant concentration or permeability distribution, must be assessed at the site.
2. Biochemical Process—Biochemical processes must be identified that will occur under conditions that can be sustained at the site and are capable of degrading contaminants of concern.
3. Delivery—Materials required to sustain degradation reactions, or microbes themselves, must be delivered to the location of the contaminants.
4. Monitoring—Subsurface conditions must be monitored to determine the location of the desired biochemical processes, and to adjust the process as required.

Biochemical processes can be identified that are capable of degrading all but the most recalcitrant compounds. However, those biochemical processes may require conditions that are challenging to achieve at many sites. For example, some chlorinated solvents can be degraded

under anaerobic conditions using biochemical processes that are currently well understood. Such conditions are common in the saturated zone, but anaerobic conditions suitable for the degradation of chlorinated solvents rarely occur naturally in the vadose zone. Experimentally, it is possible at some sites to create and sustain anaerobic conditions by infusion of high-oxygen-demand organics like lactate. In addition, some chlorinated solvents can be degraded quite effectively under aerobic conditions if a carbon source, like methane, is mixed with air and injected. (Hazen 1999b, Hazen *et al.* 1997). Correct assessment of ambient site conditions and evaluation of a feasible biochemical pathway for degrading contaminants are critical factors for successful bioremediation.

Biochemical reactions are restricted to compounds dissolved in water, and the concentration of the dissolved compounds is an important factor affecting performance. Some compounds may be toxic to microbes when present in high concentrations, even though lesser concentrations can be readily degraded. This means that bioremediation efforts cannot degrade NAPLs directly, and the high dissolved concentrations that accompany NAPL occurrence may also inhibit bioremediation. Typically, it is necessary to remove NAPLs that are floating on the water table or smearing the capillary fringe zone before biostimulation is successful (Keet 1995). This strategy greatly increases the biostimulation response time by lowering the highest concentration of contaminant the organisms are forced to transform.

The delivery of compounds to increase biochemical reaction rates is an essential part of nearly any bioremediation effort. Biostimulation and bioaugmentation have specific delivery problems, because the factors affecting transport of chemical nutrients in the vadose zone and groundwater are somewhat different from those affecting transport of organisms (Alfoldi 1988). Both bacteria and chemicals can be retarded during flow through porous materials, but even the smallest bacterium has different transport properties than dissolved chemicals. For example, the pores in clayey soils may be smaller than bacteria and physically prevent their movement, whereas this type of physical filtering never affects dissolved nutrients. Clays also may electrostatically bind negatively charged microbes, where divalent metals form cationic bridges that create a local positive charge, which will then attract microbes. Dissolved chemical nutrients also may be electrostatically attracted to the surfaces

of clay minerals, but this interaction can go well beyond simple sorption. Inorganic chemicals injected for biostimulation may precipitate metals, swell clays, change redox potentials, and modify either or both the hydraulic or electrical conductivity, all changes that can have major effects on water flow and biochemistry.

The permeability of the contaminated formation is the single most important site characteristic affecting delivery. The minimum average hydraulic conductivity is generally  $10^{-4}$  cm/sec where conventional methods are used to deliver nutrients to the saturated zone (Thomas and Ward 1989). The lower limit for successful bioaugmentation is even greater,  $10^{-3}$  cm/sec or greater, depending on the size and adherence properties of the organism being applied (Baker and Herson 1990). Recent studies have shown the less adherent strains of some contaminant-degraders can be isolated and produced to improve formation penetration (DeFlaun *et al.* 1994). Such innovations make it feasible to inject microbes into tighter formations.

Pneumatic conductivity, which decreases with increasing water content, as described in Chapter 1, affects the average delivery rate of nutrient gases in the vadose zone. Heterogeneity in the subsurface markedly affects bioremediation by influencing the flow paths of fluids or microorganisms. In general, heterogeneities cause preferential flow paths to develop so that delivery is concentrated in certain regions and avoided in others. Unfortunately, remediation will follow a similarly patchy pattern, leaving significant regions contaminated. Bedded sedimentary formations and fractured rock, or fine-grained sediments, will be particularly susceptible to this problem.

Infiltration galleries, ponding, or sprinklers are the primary method for liquid delivery to the vadose zone. Surface structures and land use prevent construction of infiltration galleries at many locations. Moreover, the flow of water from infiltration galleries downward through the vadose zone nearly always follows preferential pathways, either due to heterogeneities or from fluid instabilities at the wetting front. As a result, it is difficult (or perhaps impossible) to uniformly deliver liquids to the vadose zone where pores are partially saturated.

Delivering nutrients as a gas phase is one way to improve biostimulation in the vadose zone, largely because diffusion will smooth the irregularities in concentrations caused by preferential flow of gases much more quickly than it does in liquids. Oxygen, carbon, nitrogen,

and water can be injected as gas or vapor, and so most biostimulation in the vadose zone uses gas injection. Gaseous nutrient injection has also been used to remediate chlorinated solvents in fractured rocks at several sites (Hazen 1999a). Microbes are typically suspended in water when they are delivered, so bioaugmentation cannot use gases.

The effects of the biostimulant itself may change the permeability of the formation. Hydrogen peroxide is an excellent source of oxygen, but it can trigger such a dense growth of microbes that the pores around the injection well become plugged and block the flow of additional nutrients. Hydrogen peroxide will raise the redox potential, which may cause metals to precipitate and clog pores even further (Thomas and Ward 1989). Injecting ammonia also can be problematic because it decreases permeability by swelling clays around an injection well. Ammonia also rapidly sorbs to clays and can change the pH in poorly buffered environments.

Many of the liquid delivery problems in the vadose zone can be addressed by excavating the soil and treating it in a bioreactor, prepared bed, land farm, bioslurry reactor, biopile, or compost pile. In these cases, the permeability can be controlled or manipulated to allow better stimulation of the biotreatment process.

Where excavation is infeasible, alternative methods of delivering fluids *in situ* may improve the performance of bioremediation, particularly in formations where low permeability or heterogeneities present problems. Liquid nutrients can be injected laterally outward from a lance that is temporarily pushed into the subsurface (Siegrist *et al.* 1998). Fractures can be induced by injecting liquids or gases to increase the flow of fluids in the subsurface. Both pneumatic and hydraulic fracturing methods have been used to improve bioremediation in tight soils (Murdoch *et al.* 1994).

## Status

Biostimulation is particularly effective at petroleum-hydrocarbon degradation under aerobic conditions in the vadose zone. This application is probably the most commonly used method for treating soils containing petroleum hydrocarbons at the ground surface. Bioventing is widely used to remediate petroleum hydrocarbons because it is an effective method for low-to-moderate concentrations, and it is relatively inex-



pensive. Bioventing is used as a specific design objective, and it also can be implemented inadvertently during vapor extraction.

Bioremediation of some chlorinated solvents requires anaerobic conditions when indigenous microbes are used. It is possible to create anaerobic conditions in the vadose zone by injecting inert gas to displace air or to markedly increase the water content. However, these conditions are difficult to maintain in the vadose zone, so this process rarely is attempted above the water table. Fortunately, many chlorinated solvents can be bioremediated under aerobic conditions by addition or use of some secondary carbon source like methane, propane, or petroleum co-contaminants. Co-metabolic bioventing and biosparging has been used to cleanup a large number of sites in the last 5 years.

Genetically engineered microorganisms (GEMs) have been demonstrated to remediate polycyclic aromatic hydrogen (PAH) compounds at DOE sites in lysimeters (Ripp *et al.* 1999). The next step, still in the planning stage, is a large-scale field application at a contaminated site. This technique holds great promise for both remediation and monitoring. A large number of agricultural releases of GEMs and several bioremediations using GEMs suggest that this could become an important remediation technique, especially as the public and regulators become more comfortable with the technology.

## INJECTION OF LIQUID OXIDANTS\*

In the 1990s, *in situ* chemical oxidation emerged as a promising remediation method for sites contaminated with organic chemicals (Siegrist 1998; U.S. EPA 1998). Its promise is because many toxic organic chemicals can be either completely destroyed or partially degraded as an aid to subsequent bioremediation. Early studies were primarily focused on hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) or Fenton's Reagent ( $\text{H}_2\text{O}_2$  plus  $\text{Fe}^{+2}$ ), applied to the *ex situ* treatment of individual organic chemicals in water (Barbeni *et al.* 1987; Bowers *et al.* 1989; Watts and Smith 1991; Venkatadri and Peters 1993). Subsequent research began to explore peroxide and Fenton's reagent oxidation in soil environments (Watts *et al.* 1990; Watts and Smith 1991; Watts *et al.* 1991; Tyre *et al.*

---

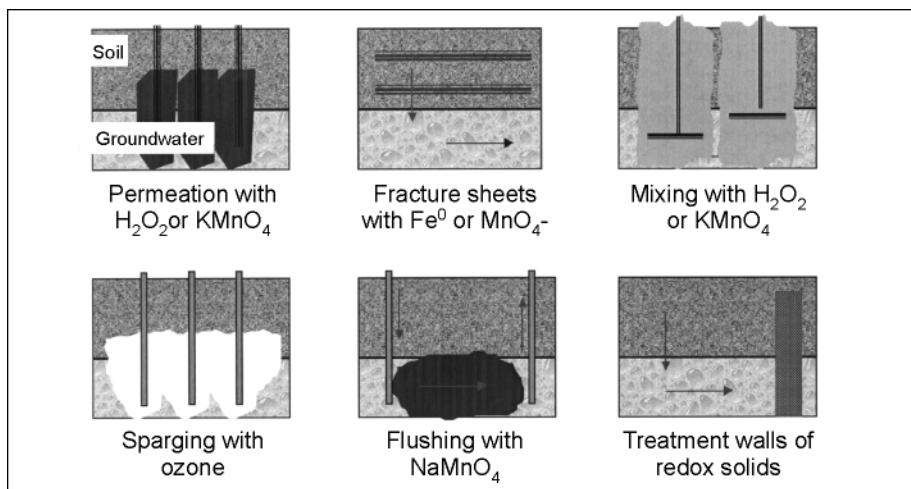
\*This section was contributed by R.L. Siegrist, O.R. West, and M.A. Urynowicz.

1991; Ravikumar and Gurol 1994; Gates and Siegrist 1993; 1995; Watts *et al.* 1997). Research was also initiated into alternative oxidants, such as ozone (Bellamy *et al.* 1991; Nelson and Brown 1994; Marvin *et al.* 1998) and potassium permanganate ( $\text{KMnO}_4$ ) (Vella *et al.* 1990; Vella and Veronda 1994; Gates *et al.* 1995; Schnarr *et al.* 1998; West *et al.* 1998; Siegrist *et al.* 1998a, b, 1999; Struse 1999). Field demonstrations and full-scale applications have evaluated alternative methods for delivering oxidants, including permeation by vertical lances (Jerome *et al.* 1997), flushing by vertical or horizontal groundwater wells (Lowe *et al.* 1999; Schnarr *et al.* 1998; West *et al.* 1998), and reactive zone emplacement by hydraulic fracturing (Murdoch *et al.* 1997; Siegrist *et al.* 1998a, b; Siegrist *et al.* 1999). This section presents the principles and practices of *in situ* chemical oxidation using peroxide and permanganate, including reaction chemistry and delivery systems. Figure 7-23 illustrates the types of systems being deployed while Table 7-4 highlights some of their key features and factors affecting performance.

Much of the research and many of the applications of liquid oxidants have been in the saturated zone. Nevertheless, there has been some important work done on vadose applications, and the technique is viable at least under some conditions in the vadose zone. One of the primary concerns with applications of this technology, or other remedial technologies where liquids are injected into the vadose zone, is the development of preferential flow paths that limit the contact between the oxidant and contaminants. These effects will be particularly important in strongly heterogeneous materials, or in coarse-grained sediments in the vadose zone where gravity dominates capillary forces. Effective methods for mitigating the development of preferential pathways, for example, by modifying well design, injection strategy, or other means, are important to the remedial performance of liquid oxidants in the vadose zone.

The case study "Case History of Liquid Oxidant Injection Into the Vadose Zone," by R.L. Siegrist, N.E. Kort, O.R. West, and M.A. Urynowicz, describes a field trial of liquid oxidant injection at the DOE Portsmouth Plant. *See page 1191.*





**Figure 7-23.** Applications of *in situ* chemical oxidation systems (Siegrist *et al.* 1999).

**TABLE 7-4**

**Features of peroxide, permanganate, and ozone oxidants as used for *in situ* remediation.**

	Features	Peroxide (Fenton's)	Permanganate	Ozone
Reagent	Form	Liquid	Liquid or solid	Gas
Characteristics	Point of generation	Offsite, shipped onsite	Offsite, shipped onsite	Onsite during use
	Quantities available	Small to large	Small to large	Small to large
Oxidation <i>In Situ</i>	Delivery Methods	GW wells, soil lances	GW wells, soil lances, fractur.	GW sparge wells
	Dose concentrations	5 to 50 wt. percent $H_2O_2$	0.02 to 4.0 wt. percent $MnO_4$	Variable
	Single / multiple dosing	Multiple is common	Single and multiple	Multiple
	Amendments	$Fe^{+2}$ and acid	None	Often ozone in air
	Subsurface transport	Advection	Advection and diffusion	Advection
	Rate reaction / transport	High or very high	Moderate to high	Very high
	Companion technology	None required	None required	Soil vapor extraction

*continued*

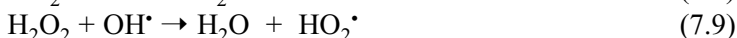
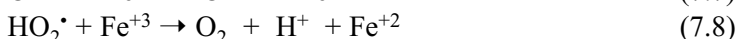
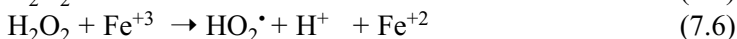
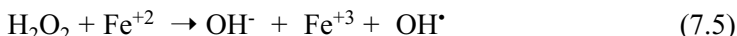
**TABLE 7-4**

**Features of peroxide, permanganate, and ozone oxidants as used for *in situ* remediation (continued).**

	<b>Features</b>	<b>Peroxide (Fenton's)</b>	<b>Permanganate</b>	<b>Ozone</b>
Oxidation Effectiveness	Susceptible organics	BTEX, PAHs, phenols, alkenes	BTEX, PAHs, alkenes	BTEX, PAHs, phenols, alkenes
	Difficult to treat organics	Some alkanes, PCBs	Alkanes, PCBs	Alkanes, PCBs
	Oxidation of NAPL	Direct oxidation possible	Direct oxidation possible	Direct oxidation possible
	Reaction products	Organic acids, salts, O <sub>2</sub> , CO <sub>2</sub>	Organic acids, salts, MnO <sub>2</sub> , CO <sub>2</sub>	Organic acids, salts, O <sub>2</sub> , CO <sub>2</sub>
	Gas evolution	Substantial gas evolution	Minimal gas evolution	Minimal gas evolution
System Effects on Oxidation	Effect of NOM	Demand for oxidant	Demand for oxidant	Demand for oxidant
	Effect of pH	Most effective in acidic pH	Effective over pH 3.5 to 12	Effective over pH 3.5 to 12
	Effect of temperature	Reduced rate at lower temp.	Reduced rate at lower temps.	Reduced rate at lower temp.
	Effect of ionic strength	Limited effects	Limited effects	Limited effects
Oxidation Effects on System	pH	Lowered if inadequate buffering	Lowered if inadequate buffering	Lowered if inadequate buffering
	Temperature	Minor to high increase	None to minor increase	Minor to high increase
	Metal mobility	Potential for redox metals	Potential for redox/exch. metals	Potential for redox metals
	Permeability loss	Potential for reduction due to gas evolution and colloids	Potential for reduction due to MnO <sub>2</sub> colloid genesis	Potential for reduction due to gas evolution and colloids

## Principles

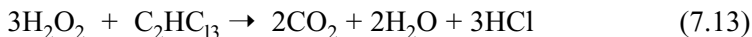
The chemical principles governing the degradation of toxic organic chemicals by peroxides were first recognized during studies focused on petrochemicals, such as naphthalene, phenanthrene, pyrene, and phenols, but later work included chlorinated solvents like TCE and tetrachloroethylene (PCE) (Watts *et al.* 1990; Watts and Smith 1991; Watts *et al.* 1991; Tyre *et al.* 1991; Ravikumar and Gurol 1994; Gates and Siegrist 1993; 1995; Watts *et al.* 1997). Oxidation using  $\text{H}_2\text{O}_2$  in the presence of native or supplemental  $\text{Fe}^{+2}$  produces Fenton's reagent, which yields free radicals ( $\text{OH}^\bullet$ ) that can rapidly degrade a variety of organic compounds (Table 7-4). However, the application of peroxide to soil and groundwater systems involves a variety of competing reactions as follows:



Hydrogen peroxide can also autodecompose in aqueous solutions with accelerated rates upon contact with mineral surfaces or carbonate and bicarbonate ions (Hoigne and Bador 1983) according to



The simplified stoichiometric reaction for peroxide degradation of TCE is

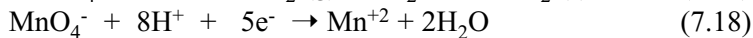
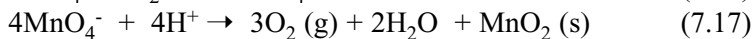
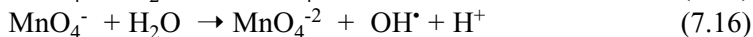
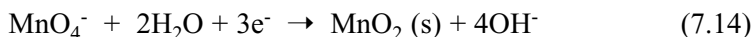


Fenton's Reagent oxidation is most effective under very acidic conditions, such as pH 2 to 4, and becomes ineffective under moderate to strongly alkaline conditions and/or where free radical scavengers like  $\text{CO}_3^{-2}$  are present. The reaction is strongly exothermic and can produce substantial gas and heat. The oxidative reactions are extremely rapid and follow second-order kinetics.

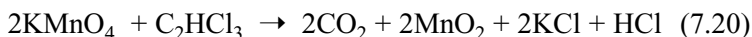
For application *in situ*, there are three processes that have been patented based on reaction chemistry and/or mode of delivery: the

CleanOX, GeoCleanse, and ISOTEC methods. While the specifics of an application will be very site-dependent, *in situ* chemical oxidation with peroxides has typically included  $\text{H}_2\text{O}_2$  concentrations in the range of 5 to 50 percent by weight and where native iron has been lacking or unavailable, ferrous sulfate is often added at mM levels. In some cases acetic or sulfuric acids are also added to reduce the pH to a more favorable acidic range. Delivery methods include common groundwater wells or specialized injectors. In many cases, multiple doses or application cycles are used to facilitate more uniform delivery of reagents and efficiency of treatment.

Compared to peroxide, oxidation of soil and groundwater using permanganate has more recently been studied for *in situ* treatment of chlorinated solvents, such as TCE, PCE, and petrochemicals such as naphthalene, phenanthrene, pyrene, and phenols (Vella *et al.* 1990; Leung *et al.* 1992; Vella and Veronda 1994; Gates *et al.* 1995; Yan and Schwartz 1996; Schnarr *et al.* 1998; West *et al.* 1998; Siegrist *et al.* 1998a,b; Lowe *et al.* 1999; Siegrist *et al.* 1999; Struse 1999). The reaction stoichiometry and kinetics in natural systems are quite complex and are not yet fully understood. Permanganate (typically as  $\text{KMnO}_4$ , but also available in Na, Ca, or Mg salts) can participate in several reactions as determined to a large degree by system pH. For example, between a pH of 3.5 and 12, permanganate ion reacts slowly to form manganese dioxide (equation 7.14). Above a pH of about 12, manganate ions ( $\text{Mn(VI)}$ ) may be formed (equation 7.15). Hydroxyl radicals may also be formed in alkaline solutions (equation 7.16). In slightly acidic solutions, the permanganate ion can decompose slowly to form manganese dioxide with a release of oxygen (equation 7.17). Below a pH of about 3.5,  $\text{Mn(II)}$  cations are formed (equation 7.18). Under acidic conditions, the permanganate ion can then oxidize the  $\text{Mn(II)}$  to form manganese dioxide (equation 7.19).



The stoichiometric reaction for the complete destruction of TCE by  $\text{KMnO}_4$  is



Under neutral or acidic pH, oxidation is speculated to occur through the formation of a cyclic ester with further reaction yielding organic acids and aldehydes as well as  $\text{CO}_2$  and  $\text{MnO}_2(\text{s})$  (Arndt 1981; Leung *et al.* 1992; Yan and Schwartz 1996). Halogenated substitution with Cl<sup>-</sup> may facilitate C-C cleavage during oxidation, although the rate of reaction slows with increasing Cl<sup>-</sup> substitution (Yan and Schwartz 1996). For example, PCE degradation is slower than TCE. The reaction appears to be second order with a rate constant of about  $0.6 \text{ L mol}^{-1}\text{s}^{-1}$  (in clean groundwater). Solution pH between 4 and 8 has little or no effect on rate, but temperature does affect the rate as described by the Arrhenius equation (Case 1997). In alkaline solutions, hydroxyl radicals may be formed and contribute to oxidative destruction (equation 7.16). The reaction can include destruction by direct electron transfer or free radical advanced oxidation. The pH of the reacting system can decline to strongly acidic conditions, such as pH 2 to 3, depending on the buffering capacity of the system. Key reaction products can include intermediate organic acids along with production of manganese oxide solids and chlorides.

Pseudo first- or second-order kinetic models often describe the kinetics of oxidant reaction with target organic chemicals. For example, during the past year kinetic studies have been completed for treatment of TCE over a wide range of concentrations (0.5 to 800 mg/L) in simulated and site groundwaters using permanganate solutions or solids at stoichiometric dosages in the range of 5x to 10x. The reaction order and kinetic parameters have been examined using pseudo first- and second-order kinetic models fit to the data:

$$\text{First order} \quad d[C_I]/dt = -k_I[C_I] \quad (7.21)$$

$$\text{Second order} \quad d[C_I]/dt = -k_2[C_I][C_2] \quad (7.22)$$

$$\text{Pseudo first order} \quad d[C_I]/dt = -k'[C_I] \quad (7.23a)$$

$$k' = k_2[C_2] \quad (7.23b)$$

where,  $d[C_I]/dt$  is rate of change in concentration of the target compound ( $\text{ML}^{-3}\text{T}^{-1}$ ),  $k_I$  is the first-order rate constant ( $\text{T}^{-1}$ ),  $C_I$  is the con-

centration of the target compound ( $\text{ML}^{-3}$ ),  $k_2$  is the second-order rate constant ( $\text{L}^3\text{M}^{-1}\text{T}^{-1}$ ),  $C_2$  is the concentration of the oxidant ( $\text{ML}^{-3}$ ), and  $k'$  is the pseudo first-order rate constant ( $\text{T}^{-1}$ ).

The degradation of TCE by  $\text{KMnO}_4$  in the absence of natural organic matter (NOM) is clearly second order, according to a series of recent tests conducted using  $\text{KMnO}_4$  solutions ranging from 0.6 to 6.3 mM. The tests determined that a second-order reaction model with  $k_2 = 0.9 \text{ L mol}^{-1}\text{s}^{-1}$  could explain the all experimental data with a relative error of only 12 percent.

The kinetics of oxidation of a given target organic chemical are also affected by matrix conditions; most notably, temperature and the concentration of other oxidant-demanding substances such as natural organic matter (NOM). Temperature effects can be described by the Arrhenius equation (Case 1997). However, the effects of NOM or minerals on the rate and extent of oxidant demand is poorly understood. Limited research suggests that the rate of oxidant consumption is comparable or slower than that of most target chemicals and that only a fraction of the total NOM is susceptible to oxidation. It is clear, however, that the rate and extent of demand must be accounted for, or a kinetic model, such as equation (7.23), will grossly over-predict the rate of destruction of a target like TCE. Moreover, if the NOM demand is high, it may deplete the oxidant and cause the reaction with the target organic chemical to cease altogether.

Another factor affecting the kinetics of destruction is the phase of the target organic contaminant; for example, whether the organic chemical is dissolved, sorbed, or occurs as a nonaqueous liquid phase. Most research has been conducted with dissolved organic chemicals. Limited research with Fenton's reagent (Tyre *et al.* 1991; Li *et al.* 1997; Watts *et al.* 1997) and permanganate (unpublished CSM work) suggests that sorption is not rate-limiting under the usual high-oxidant doses and energetic reaction conditions. Research on the oxidative destruction of nonaqueous phase liquids is limited, but preliminary results indicate that the rate of pure phase dissolution and degradation is accelerated by permanganate in the bulk solution.

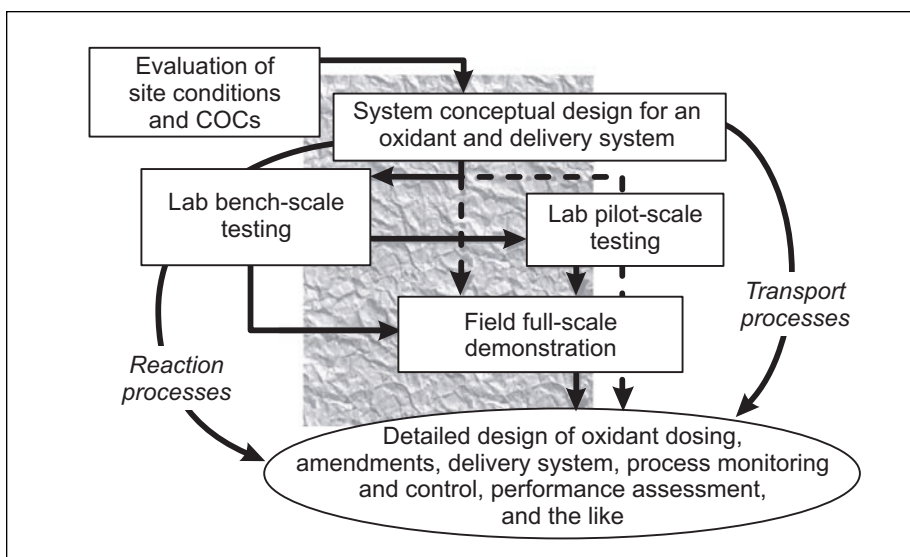
## Implementation and Augmenting Technologies

The standard of practice for the design and implementation of *in situ* chemical oxidation technologies is still evolving. While there have been



numerous laboratory studies and an increasing number of field-scale trials and full-scale projects, there are still gaps in the current knowledge base and performance deficiencies have been observed. Engineering of *in situ* oxidation technologies must, therefore, be done carefully, with due attention to reaction chemistry and to delivery and transport processes. As illustrated in Figure 7-24, the design and implementation process should rely on an integrated effort involving screening-level characterization tests and reaction and transport modeling, combined with treatability studies at the lab and field scale.

The method of delivery and distribution throughout a subsurface region is of paramount importance due to the relatively indiscriminate and rapid rate of reaction of oxidants, and it is of particular importance in the vadose zone, where preferential flow may cause the oxidant to bypass much of the contamination. Oxidant delivery systems in the vadose zone often employ infiltration galleries or injection probes. These can be coupled with delivery in the saturated zone by vertical or horizontal wells. Forced advection should be employed in both cases if permeability is adequate to rapidly move the oxidant away from the initial point of entry into the subsurface region to be treated (Figures 7-23 and 7-24). In low permeability media such as silts and clays, or when



**Figure 7-24.** Process design approach for *in situ* chemical oxidation.

oxidant reaction rates are extremely high, oxidant delivery systems can employ vertical lance injection or sparging systems, enabling high-density delivery to minimize transport distances and enhance contact with target chemicals. In contrast to peroxide and ozone oxidants, permanganate is less prone to decomposition and is more stable. As a result, it can migrate by diffusive processes, albeit at slow rates of transport (Struse 1999).

### **Critical Factors Affecting Performance**

Past experience and consideration of the current state of knowledge suggest that there are some key issues to carefully consider during design process (Table 7-5). These issues include:

- (1) The ability of the oxidant to degrade the target chemicals at a rate and to the extent required under given environmental matrix conditions.
- (2) The ability of the oxidant to be delivered to, and dispersed throughout, the contaminated region. This issue is particularly important in the vadose zone where preferential flow may limit the contact between oxidant and contaminants.
- (3) The rate and extent of natural oxidant demand.
- (4) Potential for adverse effects caused by the oxidant. Such effects include the formation of toxic by-products, gas evolution, impurities in the oxidant, precipitation of solids, permeability loss, and mobilization of metals.
- (5) Compatibility of oxidation with other technologies, like natural attenuation and post-treatment land use.

The relevance of these issues and the need for their accurate and complete delineation during system design depends on the site-specific conditions and context of the application being contemplated.

### **Monitoring**

Monitoring of *in situ* chemical oxidation in the vadose zone should be designed to verify remediation effectiveness during application, includ-

**TABLE 7-5** Representative list of organic chemicals successfully treated by chemical oxidants.

Organic contaminant	Media treated	Oxidant	References
Trichloroethylene	Water (spiked)	H <sub>2</sub> O <sub>2</sub>	Bellamy <i>et al.</i> 1991
	Silica sand (spiked)	H <sub>2</sub> O <sub>2</sub>	Ravikumar and Gurol 1992
	Silty clay soil (spiked)	H <sub>2</sub> O <sub>2</sub>	Gates and Siegrist 1995
	Sand & clay soils (spiked)	H <sub>2</sub> O <sub>2</sub> or KMnO <sub>4</sub>	Gates, Siegrist and Cline 1995
	Ground water (spiked)	KMnO <sub>4</sub>	Case 1997, Yan and Schwartz 1996
	Ground water (field site)	KMnO <sub>4</sub>	West <i>et al.</i> 1998, Schnarr <i>et al.</i> 1998
	Ground water (field site)	NaMnO <sub>4</sub>	Lowe <i>et al.</i> 1999
Tetrachloroethylene	Silty clay soil (field site)	KMnO <sub>4</sub>	Siegrist <i>et al.</i> 1999
	Water (spiked)	H <sub>2</sub> O <sub>2</sub>	Bellamy <i>et al.</i> 1991
	Silica sand (spiked)	H <sub>2</sub> O <sub>2</sub>	Leung <i>et al.</i> 1992
	Sand, clay soils (spiked)	H <sub>2</sub> O <sub>2</sub> or KMnO <sub>4</sub>	Gates, Siegrist, and Cline 1995
	Ground water (field site)	KMnO <sub>4</sub>	Schnarr <i>et al.</i> 1998
	Ground water (spiked)	KMnO <sub>4</sub>	Yan and Schwartz 1996
	Ground water (field site)	Ozone	Dreiling <i>et al.</i> 1998
Carbon tetrachloride and t-1,2-DCE	Water (spiked)	H <sub>2</sub> O <sub>2</sub>	Bellamy <i>et al.</i> 1991
Pentachlorophenol	Silica sand (spiked)	H <sub>2</sub> O <sub>2</sub>	Ravikumar and Gurol 1992
	Natural soil (spiked)	H <sub>2</sub> O <sub>2</sub>	Watts <i>et al.</i> 1990
2,4-dichlorophenol, dinitro-o-cresol	Water (spiked)	H <sub>2</sub> O <sub>2</sub>	Bowers <i>et al.</i> 1989
Trifluralin, hexadecane, dieldrin	Soil (spiked)	H <sub>2</sub> O <sub>2</sub>	Tyre <i>et al.</i> 1991
Naphthalene, phenanthrene, pyrene	Clay, sandy soils (spiked)	H <sub>2</sub> O <sub>2</sub> or KMnO <sub>4</sub>	Gates, Siegrist, and Cline 1995
Octachlorodibenzo(p)dioxin	Soil (spiked)	H <sub>2</sub> O <sub>2</sub>	Watts <i>et al.</i> 1991
Motor oil / diesel fuel	Soil (field site)	H <sub>2</sub> O <sub>2</sub>	Watts 1992
PAHs and PCP	Soil and GW (field site)	Ozone	Marvin <i>et al.</i> 1998
BTEX and TPH	Soil and GW (field site)	Ozone	U.S. EPA 1998

ing the absence of oxidation-induced adverse secondary effects. Characterization is also typically completed before application of chemical oxidation to verify suitability of the target compounds and matrix conditions, as well as to gather data to support engineering of transport and delivery methods. Remediation effectiveness is gauged by monitoring several factors: (1) oxidant distribution throughout the region of interest, (2) destruction of the target compounds, (3) production of undesirable fugitive emissions or daughter products, and (4) effects on co-contaminants, for example, redox metals. Ancillary monitoring in some applications can also include compatibility with post-oxidation processes such as bioremediation and changes in soil structure and geochemistry, which could affect subsequent land use.

Oxidant distribution can be monitored by direct measurement of oxidant concentrations, such as  $\text{MnO}_4^-$  or  $\text{H}_2\text{O}_2$ , or the reaction byproducts, such as oxygen concentrations (pore water or vapor phase), chlorides (pore water), or ions (pore water). This can be complicated in the vadose zone, but suction lysimeters can be employed for pore water sampling and soil cores can be collected by direct push technology. Alternatively, soil sensors can be employed to detect changes in soil temperature (increases), pH (decreases), or Eh (increases), one or all of which can result from an oxidant entering the vadose zone. These measurements may or may not be sensitive enough in a given setting to detect chemical oxidation in progress and they do not verify that the oxidant is still present or at a level capable of degrading the target chemicals of concern. Destruction of target compounds, such as TCE and BTEX, and production of daughter compounds, such as chlorinated alkanes or chlorinated organic acids, can be determined by either vapor phase sampling and equilibrium partitioning calculations, or by direct sampling and analysis, with great care being taken for quantification of volatile organic compounds (Siegrist and Van Ee 1994). Monitoring of fugitive gaseous emissions, of greater concern with peroxide oxidants, can be assessed by quantifying pressure gradients and/or by analysis of gas composition at key points. This can be monitored by subsurface vapor probes with pressure transducers and sampling wells, by surface flux chambers above the treated region, and/or by sampling/analysis of air within sensitive areas. This monitoring is especially critical when there are nearby conduits for untreated chlorocarbon or petrochemical gases such as sewers, utility corridors, and basements. Monitoring of any

mobile co-contaminants is normally done by direct core collection and characterization, such as speciation of chromium between  $\text{Cr}^{+3}$  and  $\text{Cr}^{+6}$  or by sampling/analysis of groundwater wells under the treated region. Ancillary monitoring is normally accomplished by soil core collection and analyses for the relevant parameters of interest.

## Status

*In situ* chemical oxidation is rapidly emerging as a viable remediation technology for mass reduction in the vadose zone as well as in the associated groundwater plumes. Tables 7-6 to 7-8 highlight several recent applications, illustrating the type of applications being pursued and the results being achieved. The oxidants most commonly employed to date include peroxide, permanganate, and ozone systems, with subsurface delivery in the vadose zone through vertical lance injectors, wells intersecting hydraulic fractures, or soil mixing techniques. In saturated zones, delivery has been achieved using vertical or horizontal wells, or sparge points.

Laboratory studies, field trials, and full-scale applications have generated considerable insight into the process, principles, and application of *in situ* chemical oxidation. In general, the oxidants have been shown to achieve high treatment efficiencies, for example greater than 90 percent, for unsaturated aliphatics like trichloroethylene (TCE) and aromatic compounds like benzene, with very fast reaction rates (90 percent destruction in minutes). Field applications have demonstrated very high reductions in the mass of contaminants, but only where adequate oxidants were able to be delivered and contacted with the target organic chemicals. These field applications have been particularly valuable in that they have clearly affirmed the control that field-scale reaction and transport processes exert on design and performance of *in situ* chemical oxidation.

The potential benefits of *in situ* oxidation include the following: (1) the rapid and extensive reactions with various COCs, applicable to many biorecalcitrant organic compounds and subsurface environments, (2) ability to be tailored to a site from locally available components and resources, and (3) facilitation of property development and transfer. Some potential limitations include: (1) requirement for handling large quantities of hazardous oxidants, (2) resistance of some COCs to oxi-

**TABLE 7-6**

**Examples of *in situ* treatment applications using peroxide**  
(after U.S. EPA 1998; Siegrist 1998).

<b>Location (date) Delivery</b>	<b>Media and COCs</b>	<b>Application method and results</b>
Ohio (1993) <i>Deep soil mixing</i>	Silty clay soil with TCE and VOCs.	<ul style="list-style-type: none"> <li>• <math>\text{H}_2\text{O}_2</math> + compressed air injected during deep soil mixing to 15 ft. depth in 3 10-ft. diam. mixing zones.</li> <li>• Up to 100 mg/kg mass reduced by 70%, including 50% due to oxidation.</li> </ul>
Colorado (1996) <i>Injectors into GW</i>	Ground water with BTEX.	<ul style="list-style-type: none"> <li>• <math>\text{H}_2\text{O}_2</math> + chelated Fe injected via 8 to 14 lances and 7 trenches over 100 ft. x 100 ft. area. Four cycles at 4 to 6 days each.</li> <li>• BTEX reduced from 25 mg/L to less than 0.09 mg/L. Property sold.</li> </ul>
Massachusetts (1996) <i>Injectors into GW</i>	TCA and VC in groundwater.	<ul style="list-style-type: none"> <li>• <math>\text{H}_2\text{O}_2</math> + Fe + acid via 2 points over 3 days within 30 ft. D.W.</li> <li>• TCA reduced from 40.6 to 0.4 mg/L, VC 0.40 to 0.08 or ND mg/L.</li> </ul>
Alabama (1997) <i>Injectors into GW</i>	Soil with high levels of TCE, DCE, and BTEX.	<ul style="list-style-type: none"> <li>• <math>\text{H}_2\text{O}_2</math> + <math>\text{FeSO}_4</math> via 255 injectors into 8 to 26 ft bgs zone of clay backfill in 2 acre waste lagoons. 120 days treatment time.</li> <li>• 72,000 lbs. of NAPLs treated down to soil screening levels.</li> </ul>
South Carolina (1997) <i>Injectors into GW</i>	Deep GW zone with PCE and TCE DNAPLs in sandy clay aquifer.	<ul style="list-style-type: none"> <li>• <math>\text{H}_2\text{O}_2</math> + <math>\text{FeSO}_4</math> via 4 injectors into zone at 140 ft. bgs beneath old waste basin. 6-day treatment time.</li> <li>• Treatment achieved 94% reduction in COCs with GW near MCLs. GW TCE reduced from 21 to 0.07 mg/L; PCE from 119 to 0.65 mg/L.</li> </ul>

**TABLE 7-7**

**Examples of *in situ* treatment applications using permanganate (after U.S. EPA 1998; Siegrist 1998).**

<b>Location (date) Delivery</b>	<b>Media and COCs</b>	<b>Application method and results</b>
Ohio (1997) <i>Horizontal well recirculation</i>	Ground water with TCE DNAPLs in a thin, sandy aquifer.	<ul style="list-style-type: none"> <li>• <math>\text{KMnO}_4</math> (2 to 4 wt.% feed) delivered by horizontal recirculation wells, 200 ft. long and 100 ft. apart at 30 ft. bags, to treat <math>10^6</math> L zone of ground water over 30 days.</li> <li>• TCE reduced from 820 mg/L to MCL in 13 of 17 wells. <math>\sim 300</math> kg of TCE destroyed. Some <math>\text{MnO}_2</math> particles generated. Aquifer heterogeneities noted.</li> </ul>
Kansas (1996) <i>Deep soil mixing</i>	TCE and DCE in soil and ground water to 47 ft. depth.	<ul style="list-style-type: none"> <li>• <math>\text{KMnO}_4</math> (3.1 to 4.9 wt.%) delivered by deep soil mixing (8 ft. augers) to 47 ft. bgs during 4 days.</li> <li>• TCE reduced from 800 mg/kg by 82% in the vadose zone and 69% in the saturated zone (<math>&gt; 8</math> ft. bgs). <math>\text{MnO}_4^-</math> depleted. Microbes persisted. Comparison tests with mixed region vapor stripping yielded 69% reduction and bioaugmentation were 38% reduction.</li> </ul>
Ohio (1998) <i>Vertical well recirculation</i>	TCE in silty sand and gravel ground water zone at 30 ft. bags.	<ul style="list-style-type: none"> <li>• <math>\text{NaMnO}_4</math> (250 mg/L) delivered by 5-spot vertical well recirculation system (ctr. well and 4 perimeter wells at 45 ft. spacing) for 3 pore volumes over 10 days.</li> <li>• TCE reduced from 2.0 mg/L to MCL. Oxidant gradually depleted in 30 days and no Microtox toxicity. No permeability loss in formation.</li> </ul>
Ohio (1996) <i>Hydraulic fracturing</i>	VOCs in silty clay soil from ground level to 18 ft. bgs.	<ul style="list-style-type: none"> <li>• <math>\text{KMnO}_4</math> grout delivered by hydraulic fracturing to create multi-layered redox zones. Emplaced over 4 days but sustained oxidative zone for more than 15 mon.</li> <li>• Dissolved TCE reduced from equiv. of 4000 mg/kg by 99% during 1 hr of contact.</li> </ul>

**TABLE 7-8**

**Examples of *in situ* treatment applications using ozone  
(after U.S. EPA 1998; Siegrist 1998).**

<b>Location (date) Delivery</b>	<b>Media and COCs</b>	<b>Application method and results</b>
Colorado (1997) <i>GW wells</i>	Soil and GW with BTEX and TPH.	<ul style="list-style-type: none"> <li>• Former gas station site. Sand/gravel to 43 ft. bgs with GW at 28 ft. 3 wells to 50 ft. depth cycling air/ozone with water recirculation. 12 cycles per day. SVE also continued. TPH in soil from 90 to 2380 mg/kg and BTEX at 7.8 to 36.5 mg/kg. TPH in GW at 490 mg/L to NAPL.</li> <li>• After 6 mon, GW below MCLs. No soils data. System shut down.</li> </ul>
Kansas (1997) <i>Injectors into GW</i>	PCE in GW.	<ul style="list-style-type: none"> <li>• Old dry cleaners site. GW at 14 to 16 ft. bgs in terrace deposits. One sparge point at 3 scfm at 35 ft. bgs. SVE wells in vadose zone. PCE in top 15 ft. of aquifer at 0.03 to 0.60 mg/L.</li> <li>• Reduced 91% within 10 ft. of well. Comparisons with air only indicated 66 to 87% reductions.</li> </ul>
California (1998) <i>Injectors into GW</i>	Soil and GW with PAHs and PCP.	<ul style="list-style-type: none"> <li>• Wood treater site 300 ft. by 300 ft. in area. Stratified sands and clays. 4 multilevel ozone injectors at up to 10 cfm. SVE wells in the vadose zone.</li> <li>• After 1 mon, PAHs at 1800 mg/kg reduced by 67 to 99% and PCP at 3300 mg/kg reduced 39 to 98%.</li> </ul>

dation, and (3) potential for process-induced detrimental effects, including gas evolution, permeability loss, and mobilizing redox-sensitive and exchangeable sorbed metals. Full-scale deployment is accelerating, but care must be taken to avoid poor performance and unforeseen adverse effects. Matching the oxidant and delivery system to the COCs and site conditions is the key to achieving performance goals. Further development work is ongoing in many areas.



## DELIVERY BY LANCE INJECTION\*

Remediation methods that rely on chemical or biological processes typically require a compound to be delivered to the subsurface. The delivery mechanism is particularly important in formations that are highly heterogeneous or that have a low permeability. Delivery systems that can inject materials at closely spaced locations can facilitate remediation in these settings. Specialized drilling systems, or lances, have been developed to rapidly permeate a formation with treating compounds. This technique is also called “lance permeation.”

### Principles

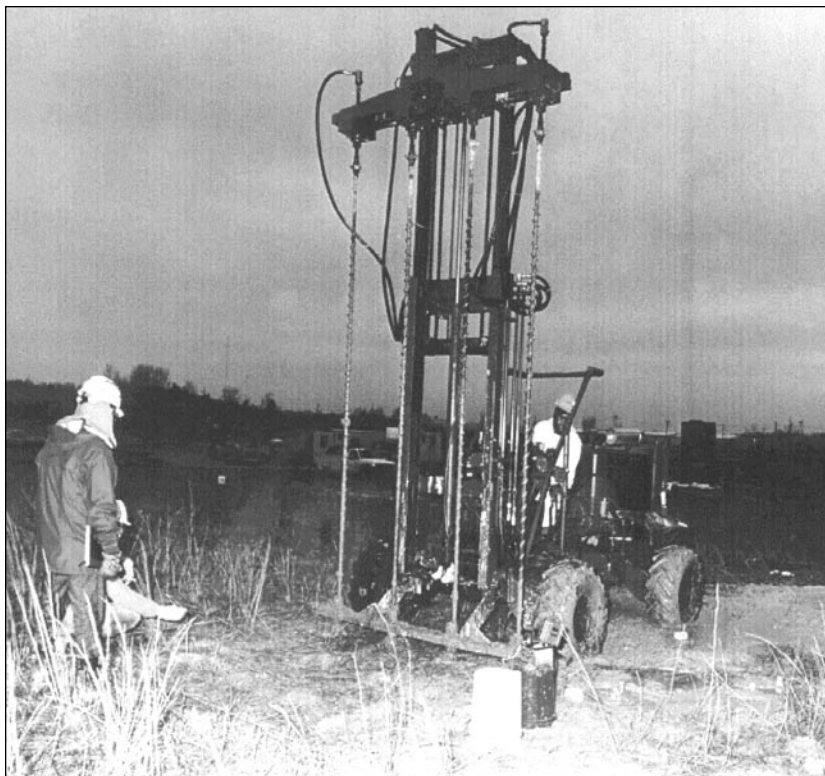
Lance permeation involves advancing small augers, or directly pushed casing, while injecting one or more reagents. The reagents migrate away from the lance by entering existing pore and fracture networks and creating a halo of reactivity. Slower diffusion processes can supplement this advective movement. To ensure complete coverage in a particular region, the lance injections are made with relatively close spacing, typically within 0.6 to 1.2 m of each other.

A particularly effective apparatus for this type of delivery consists of as many as four narrow augers mounted side-by-side on a frame attached to a tractor (Figure 7-25). The unit is mobile and can penetrate up to 10 m below the ground surface, with fluid flowing from all four augers simultaneously. Other equipment, such as cone penetrometers or GeoProbe™s, use static weight or hammers to push pipes that have been used as injection lances. The direct-push equipment generates less waste, and it can penetrate deeper than the multi-auger device. The simultaneous use of four augers, however, causes the multi-auger system to deliver reactive compounds considerably quicker than direct-push equipment. For this reason, much of the work described here will focus on applications of the multi-auger system.

The typical approach has been to inject, at relatively low pressures, 200 to 500 kPa (2 to 5 atm) to fill pores with injected fluid but avoid hydraulic fracturing. Agents can be injected up to the air-filled porosity of the media, but might be constrained in the range of 5 percent v/v. The

---

\*This section was contributed by R.L. Siegrist.



**Figure 7-25.** *In situ* reagent delivery using tractor-mounted multiple lance equipment.

following agents have been delivered under field trials or full-scale applications: (1) tracers that evaluate uniformity of delivery, (2) an alkaline slurry that increases soil pH and immobilizes metals, (3)  $\text{KMnO}_4$  and  $\text{H}_2\text{O}_2$  that oxidatively degrade organic chemicals, (4) zero-valent iron metal that reductively degrades chlorinated solvents, and (5) bionutrients that stimulate indigenous microbes and enable bioremediation of organic chemicals. In addition, compressed air has been injected at somewhat higher pressures to increase pneumatic permeability and facilitate soil vapor extraction.

Existing applications have injected fluid at relatively modest pressures, but an application scheduled for future deployment at the DOE Portsmouth Gaseous Diffusion Plant will utilize a somewhat different

approach. High pressure (50 to 100 MPa), low-flow jets will be used to carry reactive fluids away from a lance that is pushed into a low-permeability formation. This approach is expected to increase the radius that can be quickly permeated by a single bore.

## **Implementation**

The implementation of lance permeation technologies relies on available equipment, treatment processes that are selected for the specific contaminants, and environmental conditions at the site. Site physical conditions need to be examined to ensure the proper penetration depth is possible and that the volume of fluid to achieve a treatment effect can be delivered. It is important that the contaminants of concern and the desired treatment goals be defined. Batch experiments with the site media and contaminants, along with the treatment agents to be employed, can reveal rate and extent of reaction data. Data gathered from diffusive transport tests in the lab reveal important information about real transport rates, extents, and any matrix interactions. A field pilot test is often required to verify laboratory results and field performance.

## **Critical Factors Affecting Performance**

The contaminant and the deposit are singular factors affecting performance, but the interaction of the two also must be taken into consideration. Central among these issues is the flow of liquids injected by the lancing technique. In coarse-grain deposits, injected liquids may form unstable fingers that move rapidly downward and extend outward to limited distances. Jetting may help extend the radius of influence, and closely spaced injection points will reduce the volume of fluid injected into any particular location, but unstable flow or the development of preferential paths may limit the contact between reactive fluids and the contaminant.

If the formation is extremely tight, then dispersal using low pressure lance permeation may be ineffective. Some degree of advection away from the lance is important to yield a rapidly evolving halo around the lance. However, there are some advantages to applications of lance permeation methods in fine-grained formations. In fine-grained deposits, diffusive transport can expand and homogenize the treated region.

Moreover, capillary forces will dominate gravitational forces affecting fluid flow in fine-grained formations, and this will limit the effects of preferential flow.

The formation must be sufficiently unconsolidated and free of boulders or buried debris, such as underground utilities and conduits, so that a lance can penetrate the desired depth. None of the lance permeation techniques will work in crystalline rock. Surface obstructions, such as parking areas and buildings, preclude application or greatly increase costs. If contaminant concentrations are too high, the mass of treatment agent that can be delivered in the volume of fluid may be insufficient and may require multiple treatment cycles. The ability to retreat or increase delivery in hot spot areas is an advantage of multipoint lance injection. The groundwater zone and its susceptibility to contamination by leaching of contaminants or treatment agents during permeation of the overlying vadose zone must be considered.

## Monitoring

Monitoring requirements include: (1) reagent delivery volumes and pressures, and depth of delivery, (2) subsurface biogeochemistry changes important to the treatment being implemented, and (3) changes in contaminant mass or mobility within the region treated. Available sensing devices and data acquisition systems perform monitoring. Soil core samples, which are used to analyze target constituents and relevant properties, can be acquired by direct push technology. Even with the monitoring technology to date, inaccurate quantification of treatment efficiencies in low permeability and heterogeneous systems still exist, and error and uncertainties, regardless of sample numbers, remain unacceptably high.

## Status

Field trials involving multiple reagents were evaluated by Siegrist *et al.* at the DOE Portsmouth Gaseous Diffusion Plant beginning in 1994. A field trial in California evaluated lance injection and permeation dispersal of  $\text{KMnO}_4$  to treat trichloroethylene in massive soils to a depth of 10 m. A site in Ohio contaminated by TCE and other halocarbons is com-

pleting a field test during 1999. Information to date suggests a treatment cost on the order of \$25 per c.y., somewhat independent of reagent costs.

### INJECTION OF GAS-PHASE OXIDANTS: OZONE GAS\*

Ozone ( $O_3$ ) gas is a strong oxidizer (oxidation potential of 2.07 volts) that will degrade a variety of organic compounds. It is used to destroy organic contaminants in drinking water, wastewater, marine aquaria, and swimming pools. Recently, ozone has been injected into the subsurface to remediate recalcitrant organic contaminants *in situ*. Ozone can be injected directly into wells in the vadose zone, or it can be sparged into wells screened in the saturated zone. The gas is injected into pore spaces to contact contaminants, which are then degraded to daughter compounds. The technology has been used to treat regions containing dissolved, sorbed, and NAPL-phase contaminants, including pentachlorophenol (PCP) and polynuclear aromatic hydrocarbons (PAHs) (Fluor Daniel GTI 1998; Marvin *et al.* 1998; Brown *et al.* 1997; Nelson *et al.* 1997), and chlorinated solvents trichloroethene (TCE) and dichloroethene (DCE) (Clayton and Nelson 1995).

*In situ* ozonation may have several advantages over other oxidant-injection methods at some sites. The most significant advantage is that the gaseous nature of ozone promotes delivery through the vadose zone more readily than that of liquid oxidants. Volatilization and subsequent oxidation of residual NAPL may also occur during gas injection. Since ozone contains only oxygen atoms, it may impose less geochemical stress on the subsurface environment than oxidants containing ionic species such as  $Fe^{2+}$ ,  $K^+$ ,  $Na^+$ , or  $MnO_4^-$ . For this reason, ion exchange and solids precipitation are generally minimal during ozonation.

There can be significant limitations to *in situ* ozonation, primarily related to subsurface ozone transport, and competition for consumption among natural organic matter and other oxidizable species. While these limitations are common to all *in situ* oxidation technologies, they are expressed uniquely for each technology.

Managing the application of *in situ* ozonation involves the following primary issues: (1) determining that oxidation by ozone is a feasible

---

\*This section was contributed by W. Clayton.

treatment mechanism for the specific contaminants, (2) delivering an appropriate mass of ozone to ensure complete treatment, and overcoming competing ozone consumption, such as by natural organic matter, (3) providing adequate subsurface transport of ozone gas so that injected ozone contacts all contaminated areas, and (4) implementing appropriate engineering and safety controls for ozone gas generation and handling.

The case study "Vadose *In Situ* Ozonation of Polynuclear Aromatic Hydrocarbons and Pentachlorophenol," by Wilson S. Clayton, describes an application of *in situ* ozonation in Sonoma County, California. See page 1200.



## Treatment Mechanisms

*In situ* ozonation involves three primary treatment mechanisms: (1) direct oxidation, (2) advanced oxidation, and (3) combined chemical-biological oxidation. These mechanisms are interrelated and they can be difficult to distinguish in detail, even in carefully controlled aqueous- or slurry-phase reactors. A full understanding of these treatment mechanisms is particularly difficult in the subsurface, where geochemical reactions can be poorly resolved. The many possible interactions between contaminants, ozone, and native aquifer are poorly understood from a mechanistic viewpoint. Therefore, most of the generalizations about the treatment mechanisms are made by reference to the water treatment literature, and by observations from bench tests and *in situ* ozonation project sites.

Laboratory testing of ozone treatability is critical to determine site-specific feasibility. This testing is important despite published literature and previous experience and results to guide expectations. Ozone treatability work should include either slurry tests or column tests to account for the effects of soil matrix interactions. Laboratory treatability tests are especially critical for contaminant mixtures, where specific compounds may be preferentially oxidized.

### Direct Oxidation

Contaminants susceptible to direct oxidation by ozone are generally organic chemicals that contain carbon-carbon double bonds (Rice and Browning 1980). Examples of double-bonded organics that should be read-

ily treatable by direct oxidation using ozone include: (1) nitroaromatic explosive compounds such as TNT, DNT, TNB, DNB, and tetryl, (2) aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylene (BTEX), (3) PAHs such as benzo(a)pyrene, naphthalene, and pyrene, (4) vinyl chloride, (5) chlorinated ethenes such as DCE, TCE, and PCE, (6) phenols, and (7) chlorinated phenols such as PCP and dichlorophenol.

The oxidation of a complex organic molecule has factors affecting intermediate compounds. Research has shown that intermediate compounds are readily oxidized if sufficient ozone is delivered. For example, Qiu *et al.* (1999) studied the oxidation of DCP by ozone, showing that intermediate chlorinated compounds were further oxidized to produce chloride, acetic acid, and ethylacetate. The acetic acid and ethylacetate can be readily biodegraded under aerobic conditions, resulting in complete mineralization of the contaminant.

### **Advanced Oxidation**

Ozone may form hydroxyl radicals (AOH) as a second reaction pathway. These can be produced by the decomposition of ozone in the presence of water or enhanced by addition of radical promoters such as hydrogen peroxide ( $H_2O_2$ ). Oxidation by AOH is faster and more aggressive than direct oxidation by ozone, and can address a wider range of organic contaminants (Hoigne and Bader 1976). However, the degree of AOH produced during *in situ* ozonation is difficult to measure and is small to moderate unless  $H_2O_2$  is added.

### **Combined Chemical-Biological Oxidation**

*In situ* ozonation may enhance aerobic biodegradation, although the details of this process are still being resolved. Ozone degrades to oxygen gas, so the by-product of ozonation can provide an important ingredient for aerobic biodegradation. However, ozone is a powerful sterilizing agent with the capacity to destroy the microbes involved with aerobic degradation. This sterilizing potential apparently is incompletely realized, because unpublished field and laboratory data indicate that significant microbes survive and will flourish after cessation of ozone injection. Ozone may be unable to penetrate and sterilize the myriad pore spaces housing bacteria in the subsurface. Other research (Brown *et al.* 1997) suggests that ozone can transform some recalcitrant

contaminants into readily biodegradable daughter compounds, which may further enhance bioremediation.

### **Ozone Mass Delivery**

Ozone consumption under both laboratory and field conditions appears to range from 3 to 10 grams of ozone per gram of organic contaminant, according to unpublished studies conducted by the author. These values include ozone demand by oxidizable native aquifer materials, such as humic matter or carbonates, although data are unavailable for materials with a wide range of naturally occurring organic material. Certainly, the mass of ozone required to completely oxidize contaminants in formations rich in native organic material, such as peat, lignite, or some shales, would be excessive. Bench-scale studies can be conducted to evaluate the ratio of the mass of ozone consumed to the mass of contaminants degraded in a particular material.

### **Ozone Transport and Mass Transfer**

*In situ* oxidation will generally rely on effective transport of the oxidant to the contaminant. This is a contrast to many *in situ* remediation technologies that rely on mobilization and extraction of contaminants. For ozone injection, ozone reactions and mass transfer from the gaseous phase to the aqueous phase exert critical control over the ability to contact target contaminants.

A general conceptual model for ozone transport begins when ozone gas is transported by advection within gas-filled pores in the subsurface. It is then lost to the aqueous phase by mass transfer and reactions in all phases. The net result is the decrease of ozone concentrations along the flow path. Clayton (1998) used this conceptual model to develop an unsteady state numerical model of ozone and contaminant mass transfer and transport phenomena. The results of this modeling effort show that ozone degradation limits ozone transport, even in the absence of contaminants or other oxidizable material. During the early phase of treatment, second order reactions between ozone and contaminants or other oxidizable material near the injection well can deplete ozone gas concentrations. As contaminants and native materials near the injection well are oxidized, ozone gas is transported farther. Changes in ozone gas



distribution over time are controlled by the balance between gas flow velocity, and mass transfer and reaction rates. Increased ozone injection flow rates and concentrations help transport ozone farther. Ozone transport distances are also sensitive to the effective air saturation as a smaller effective air saturation results in a greater advective velocity and greater ozone transport distances.

In addition to the limitations on ozone transport imposed by ozone reactivity, subsurface heterogeneity can lead to preferential flow of injected gases in high permeability zones. In a severe case, advective gas flow avoids the low permeability zones. Ozone transport into the low permeability zones is then limited by diffusion, either in the gas phase or the aqueous phase.

In heterogeneous environments, geologic control over ozone transport is a primary design consideration. Injection well spacing and screened intervals should be selected based on careful geologic characterization. Multi-level injection wells may be required in some settings to obtain adequate ozone transport. Subsurface monitoring should also allow for the accurate characterization of the distribution of ozone in the gas phase and aqueous phase.

### **Engineering and Safety Controls For In Situ Ozonation**

The engineering design of an *in situ* ozone injection system requires that the following criteria be met: (1) the ozone generator system must deliver a sufficient amount of ozone to destroy the required contaminant mass within a target time, (2) the system must deliver the ozone gas at sufficient pressure and flow to achieve adequate subsurface ozone transport, (3) the system must be constructed of materials which are chemically resistant to degradation by ozone, and (4) the system must include sufficient safety control systems to ensure that site personnel are protected from possible physical hazards and releases of liquid oxygen or ozone gas.

Ozone gas is created onsite using an ozone generator, which exposes oxygen to a high voltage electrical discharge. Ozone can be generated from air or from pure oxygen. Use of air typically generates an ozone concentration of about 1 percent, whereas use of pure oxygen as feed gas typically results in ozone concentrations of 4 to 6 percent.

Ozone generators typically operate within a narrow range of pressure and flow. Ozone gas distribution header systems must allow for independent pressure and flow control on multiple injection legs. This allows ozone injection at discrete pressures and flow rates in different injection points to accommodate heterogeneous environments.

Materials involved in the ozone delivery system should be constructed of Teflon or stainless steel. Alternate materials may be acceptable for components with limited ozone contact. Engineered safety controls should include system interlocks to shut down ozone generation in the event of a leak of ozone or oxygen gas.

Control and monitoring of subsurface gases is critical for safely implementing ozone injection. Impermeable covers and extraction vents can be used to maintain control of the injected ozone. Monitoring the pore gas compositions, both within and outside of the treated area, is also important to ensure that fugitive emissions of ozone are avoided.

## **Status**

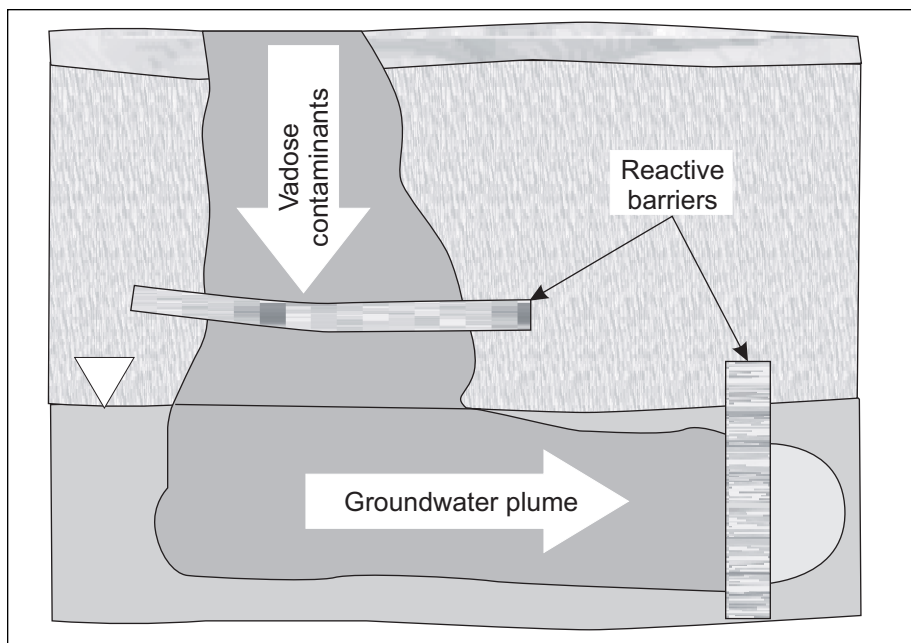
The general applicability of ozone injection has been established through several professional reports and non-peer-reviewed papers describing remedial action projects. The field demonstrations performed to date have focused on meeting remediation objectives for industrial clients, which has precluded obtaining detailed data typical of research projects. However, the results have been encouraging and this technology shows promise. Current experience with this new technique is limited to a few consulting companies.

## **REACTIVE BARRIERS\***

Vertical reactive barriers have recently become a widely accepted method for remediation of dissolved contaminants in horizontally moving groundwater plumes. A companion technology has been developed that uses horizontal reactive barriers to degrade vertically moving contaminants in the vadose zone (Figure 7-26), but it has lagged behind

---

\*This section was contributed by L.C. Murdoch and W.W. Slack.



**Figure 7-26.** Reactive barriers in the vadose and saturated zones.

applications in the saturated zone. Research into the use of horizontal reactive barriers has indicated that they could have an important place in the search for increased remedial effectiveness at reduced costs.

The basic remedial approach using a reactive barrier, whether above or below the water table, is to first build a structure in the subsurface that will intercept the entire cross section of flowing contaminated water. Special material that will degrade or even immobilize contaminants on contact is placed in the structure, and the natural hydrologic system equilibrates. The barrier may contain impermeable panels to divert the subsurface flow, but the actual reactive zone is typically as permeable as the enveloping aquifer to ensure that water will flow through the material and not be diverted around it. When functioning properly, contaminants are carried by the ambient flow of water into the reactive zone where they are removed. Clean water emerges from the downstream side of the zone allowing water to pass unrestricted and barring the migration of contaminants. Orientation is a major difference between reactive barriers in the vadose zone and those in aquifers. Reactive barriers in the

saturated zone are typically vertical and positioned normal to the azimuth of ground water flow, whereas those above the water table must be nearly horizontal to intercept the predominantly downward moving water in the vadose zone.

The strategy for using reactive barriers is markedly different from most other methods that seek to reduce risk by removing or destroying all contaminants. Instead, reactive barriers are intended to degrade contaminants that are mobile, while having little effect on immobile compounds. Risk is reduced by placing reactive barriers upstream from potential receptors. The barriers prevent mobile contaminants from reaching receptors, but immobile contaminants may be left in place. In the vadose zone, reactive barriers are largely intended to intercept downward moving contaminants before they reach the water table where they could flow to a well or stream. Interestingly, soluble reactive compounds used in reactive barriers may diffuse through the vadose zone and destroy some compounds before they are mobile (Siegrist *et al.* 1999).

Several types of reactions can be used in barriers including aggressive chemical degradations, milder biochemical transformations, and sorption reactions. Zero-valent iron is currently the most widely used compound in reactive barriers in the saturated zone and has also been used above the water table (Table 7-9). Potassium permanganate is an aggressive oxidant that will degrade many organic compounds, although

TABLE 7-9	Some reactive materials, their mechanism of degradation, and the type of contaminant that could be degraded in a reactive barrier.	
Reactive Material	Mechanism	Target Contaminant
Zero-valent iron	Reductive dechlorination	Chlorinated solvents
Potassium permanganate	Oxidization Sorption	Organic chemicals, metals
Porous ceramic	Bioremediation	Hydrocarbons, solvents
Manganese peroxide	Aerobic biodegradation	Hydrocarbons
Sodium percarbonate	Aerobic biodegradation	Hydrocarbons
Lactate or similar	Anaerobic biodegradation	Solvents
Activated carbon	Sorption	Metals +/- Organics
Surface modified zeolite	Sorption	Metals

applications thus far have targeted chlorinated solvents. Manganese oxide produced when permanganate is reduced will sorb metals or radionuclides to the reactive barrier. This sorption suggests that this material may form a barrier suitable for mixed wastes. Porous ceramics are well suited as host media for microbes used to facilitate bioaugmentation. Manganese peroxide and sodium percarbonate are solid peroxides that react with water to release oxygen. They fuel aerobic biodegradation reactions, particularly of petroleum hydrocarbons. Lactate or similar compounds are used to enhance anaerobic reactions designed to degrade chlorinated solvents. Lactate and the peroxides are highly soluble in raw form, so they are processed with insoluble binders to delay their release. Granular activated carbon and surface-modified zeolites will sorb contaminants and are suitable for use in reactive barriers where immobilization is advantageous. For example, sorbants could arrest the migration of metals or radionuclides.

Reactive barriers must be thick enough to sufficiently degrade contaminants while they are in contact with the reactive material. Increasing thickness will increase material costs, which can be a significant component of the project cost. Barrier thickness can also influence implementation or method of construction. Determining the thickness required for a reactive barrier involves balancing the water flux and concentration of contaminants flowing into the barrier with the thickness and rate of degradation in the barrier itself. Many degradation reactions are essentially first order, where the reaction rate is proportional to the concentration of contaminants. Assuming that water is flowing normally to the barrier, and the vertical flow rate is uniform through the barrier, the concentration profile through the reactive barrier is

$$\frac{C}{C_o} = \exp \left\{ \frac{-S_w \phi_e k}{v_w} \right\} x \quad (7.24)$$

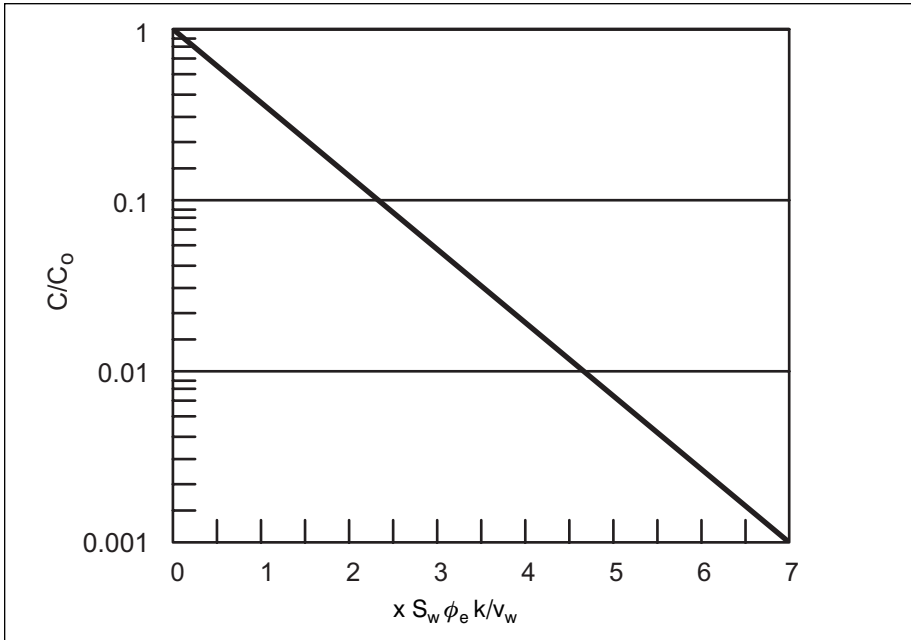
where  $C_o$  is the concentration entering the barrier,  $k$  is the first order constant of the decay reaction,  $v_w$  is the flux of groundwater in the  $x$  direction perpendicular to the barrier, and  $\phi_e$  and  $S_w$  are the effective porosity and degree of water saturation of the barrier material, respectively. The concentration through the barrier will decrease as a negative exponential with distance (Figure 7-27), according to this simple analysis. Equation 7.24 can determine how thick the barrier should be to

reduce the incoming concentration by a certain fraction. The thickness required to reduce the concentration by one order of magnitude ( $C/C_0 = 0.1$ ) is from equation (7-24) and Figure 7-27.

$$X_{0.1} = 2.3 \frac{v_w}{\phi_e S_w k} \quad (7.25)$$

Reducing a concentration in groundwater by two orders of magnitude ( $C/C_0 = 0.01$ ) will require a reactive barrier twice as thick as indicated by equation 7.25. This relation (equation 7.25) shows that the thickness of a reactive barrier is directly proportional to the flux, and it is inversely proportional to the effective porosity and the reaction rate.

Equation (7.25) can be used to estimate thicknesses required for reactive barriers. The half-life of degradation reactions ranges from a few minutes for potassium permanganate to a day or longer for zero-valent



**Figure 7-27.** Concentration as a function of distance, reaction rate, effective porosity and flux through a reactive barrier. Assuming first-order decay reaction and flow in the positive  $x$  direction.

iron or other compounds. Expect from this that  $k$  will range from less than  $10^{-5}$  to  $10^{-3} \text{ s}^{-1}$ . The average flux through the deep vadose zone is the rate at which the underlying aquifer is recharged. Recharge fluxes are on the order of  $10^{-6} \text{ cm/s}$  in the eastern United States, but they could be 2 orders of magnitude less ( $10^{-8} \text{ cm/s}$ ) in arid regions of the west, such as Sandia or Hanford. The effective porosity of reactive material that is granular is probably at least 0.15. Using those values and equation (7.25), the thickness of a reactive barrier required to reduce concentrations by a factor of 10 ranges from  $10^{-4} \text{ cm}$  for the fastest reactions and the slowest recharge flux to 1.5 cm for the slower reaction and the faster recharge flux. Those thicknesses would be doubled to reduce concentrations by a factor of 100.

The design considerations presented in the previous paragraphs have assumed that the water flow through the barrier is uniformly distributed; however, it is widely recognized that flow through the vadose zone can be localized along preferential paths. Certainly the occurrence of fast, localized flow through a barrier will reduce the residence time and change the thickness calculations based on equation (7.25). The severity of this issue is unclear, but probably depends on the permeability structures of the host formation and reactive barrier material, as well as the maximum water flux applied to the barrier. It should be feasible to use principles for capillary barriers to design the hydraulic properties of a material that would impede flow along a fast path long enough to ensure degradation. Of course, this would have to be done without excessively impeding flow and diverting water around the barrier. The details of this process have never been investigated with respect to reactive barriers in the vadose zone, but they should be amenable to available experimental and theoretical techniques.

## Implementation

The two major issues affecting reactive barrier implementation in the vadose zone are: (1) constructing a barrier at the required location and (2) selecting a material that will safely treat the contaminants. Barrier construction requires creating a flat-lying layer of reactive material in the subsurface. Several methods based on horizontal wells have been proposed. Material can be permeated, or sediment can be eroded with a high-pressure jet to create panels between parallel horizontal wells (Sass

*et al.* 1997). A mechanical device has also been used to cut the formation between horizontal wells (Carter 1997). High pressure jets may be deployed from vertical wells to create flat-lying disk-shaped bodies in the subsurface. A continuous layer can be formed from this deployment by creating many neighboring disks at the same depth (Furth *et al.* 1997). Those methods typically have been used to create low permeability barriers, but they apparently have not been used to create permeable barriers from reactive material.

Hydraulic fracturing is another method for creating gently dipping layers of granular material, and, as far as is known, it is the only one that has been used to create reactive barriers in the vadose zone.

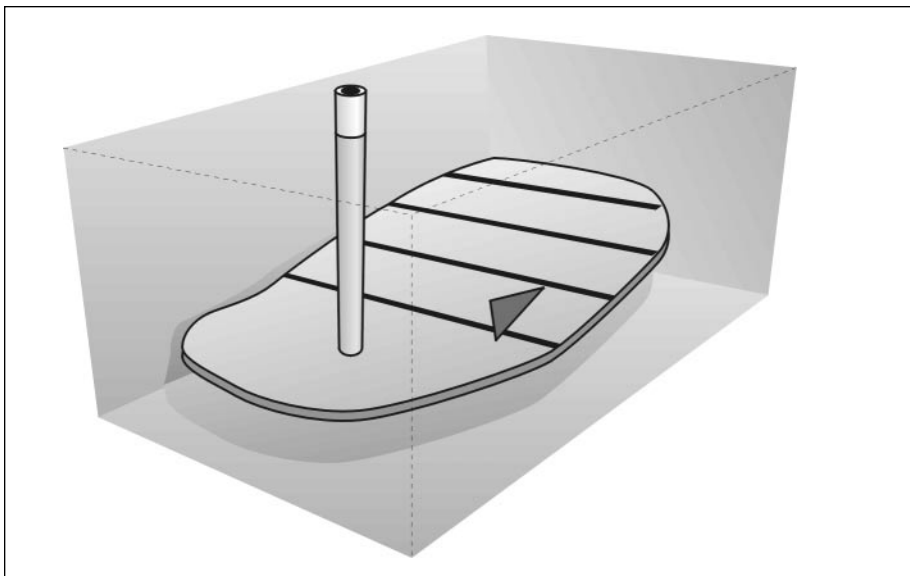
Hydraulic fracturing begins by injecting fluid into a borehole until the pressure exceeds a critical value and a fracture is nucleated. Granular material is injected as a slurry while the fracture grows away from the borehole. A viscous fluid, typically either an organic or inorganic gel, is used to facilitate transport of the granular material into the fracture. After pumping, the fracture walls close on the granules to form a thin layer or bed of reactive material in the subsurface (Murdoch *et al.* 1995).

Conventional methods of hydraulic fracturing generally produce a single parting (multiple fractures require repeated operations), and the form of the fracture depends on the state of stress, the degree of stratigraphic layering or fabric in the enveloping formation, and may include other factors. In overconsolidated or bedded sediments, hydraulic fractures, typically, are equant to slightly elongate in plan, and dip gently towards their parent borehole (Figure 7-28).

Hydraulic fractures have been created for environmental applications at depths of 12 and 16 m with the possibility of greater depths. Many of those fractures have been created in the vadose zone. Maximum dimensions of the fractures increase with depth, but are in the range of 7 to 15 m. Bulk volumes of granular material used to fill the fractures also increase with depth, ranging from 0.15 m<sup>3</sup> (5 ft<sup>3</sup>) for shallow fractures to 1.25 m<sup>3</sup> (44 ft<sup>3</sup>) for deeper ones. The average thickness of material filling a fracture ranges from 0.5 to 1.0 cm, but can be as much as 2.5 cm. Special methods (Brunsing 1987; Murdoch *et al.* 1997) are available to create fractures that are a decimeter or more thick.

Hydraulic fracturing methods have created reactive barriers in the vadose zone using most of the materials in Table 7-9. Lactate and zeolite are two exceptions only because environmental applications of those





**Figure 7-28.** Idealized hydraulic fracture.

materials are relatively new. Conventional fracturing methods can be used to inject many reactive materials. Guar gum gel, a cellulose-based thickening agent, is typically used to suspend reactive material, although this gel is abruptly degraded by the oxidative capacity of raw potassium permanganate. An inorganic gel is used to inject potassium permanganate (Siegrist *et al.* 1999).

The case study, "Case History of Reactive Barriers Using  $\text{Fe}^0$  Metal and  $\text{KMnO}_4$  to Degrade Chlorinated Solvents," by R.L. Siegrist, K.S. Lowe, L.C. Murdoch, and T.C. Houk, describes a field trial of *in situ* remediation at the DOE Portsmouth Plant. See page 1206.

## Monitoring

Reactive barrier monitoring in the vadose zone evaluates the creation of the barriers, as well as their performance. Determining the form of the fracture, particularly the size and location, is critical to ensuring that

potential downward pathways of contaminants are intercepted. This can be done using geophysical methods during or following fracturing. The ground surface over a flat-lying hydraulic fracture will lift to form a broad, gentle dome. The amount of uplift is similar to the fracture aperture above shallow, flat-lying fractures (Murdoch *et al.* 1995), but the uplift pattern becomes more complicated as the fracture becomes deeper. Theoretical analyses are available to estimate the geometry of hydraulic fractures based on the uplift pattern (Du *et al.* 1993; Davis 1983). Net ground displacements accompanying fracturing can be measured using optical leveling, or the inclination of the ground surface can be measured in real time using an array of tiltmeters. Resistivity measurements can also be used to estimate fracture location during propagation (Wang *et al.* 1991; G. Hocking, personal communication, 1998).

The performance of reactive barriers in the vadose zone can be evaluated using the standard vadose zone sampling and monitoring methods described in Chapters 3 and 4. Specialized methods (Murdoch *et al.* in press) have been developed to monitor critical parameters, such as moisture content, Eh, or fluid composition, at closely spaced depth intervals. Sensors can be embedded into a borehole sidewall at spacings of as little as 7 cm, to provide detailed resolution of subsurface processes.

### **Factors Affecting Performance**

Reactive barriers must be able to intercept contaminants and provide enough residence time to accomplish sufficient degradation. The two primary factors that will affect these processes are the orientation and position of the barrier, and the properties of flow through the barrier. Reactive barriers in the vadose zone should be nearly flat-lying to intercept downward flow. The dip of barriers created using hydraulic fracturing methods depends largely on the state-of-stress and sediment anisotropy. A lateral compressive stress that is greater than the vertical compressive stress favors the creation of a flat-lying fracture because it is easier for the dilating fracture to lift against the vertical than to push against the lateral stress. This stress state occurs in over-consolidated sediments and many rocks.

Material anisotropy, particularly the fracture toughness, becomes important where the horizontal and vertical stresses are similar. Fracture toughness is the property that governs the propagation of an elastic

fracture, and it often differs with direction in natural materials. For example, some sediments part more readily parallel to bedding than they do perpendicular to it because the least fracture toughness is parallel to bedding. As a result, bedding planes or laminations may favor the creation of flat-lying hydraulic fractures in sediments where the vertical and horizontal stresses are similar, such as in normally consolidated sediments.

Reactive barriers must be capable of degrading contaminants while they reside in the reactive material. The simple approach outlined above indicates that for a sufficient residence time to elapse, the thickness of reactive barriers in the vadose zone should be at least a few mm to cm, and this thickness is readily achieved by hydraulic fracturing methods. However, it is likely that local fluxes could be markedly greater than the average yearly flux used in the calculations above. For example, this could occur if the contaminants move episodically along permeable paths in heterogeneous formations, or as unstable fingers in granular deposits. Little is known about the details of flow through reactive material in the vadose zone, so this issue remains unresolved. It may be possible that concepts developed for designing capillary barriers could be used to design material properties that would regulate flow through reactive barriers in the vadose zone.

Access to the subsurface is required to create a reactive barrier. Conventional drilling is typically used, but hydraulic fractures can be created using directional drilling when access by conventional rigs is impossible. Buildings or other structures overlying fractures should be capable of accommodating some displacements during the fracturing process.

The rate of the degradation reaction and the life of the reactive material affects the performance of the barrier. These issues depend on details of the type, concentration, and total mass of the contaminants in the vadose zone, as well as the subsurface geochemical setting. Materials are available to degrade or sorb many of the major contaminants (Table 7-9), and current information about their performance in the vadose zone is encouraging (Siegrist *et al.* 1999). However, only a handful of field trials have been attempted, so additional investigation is required before the scope of these factors can be assessed.

## Status

The use of reactive fractures in the vadose zone is a new technology with only a handful of field examples. Flat-lying reactive barriers suitable

for the vadose zone have been created using granules of potassium permanganate, zero-valent iron (Siegrist *et al.* 1999), porous ceramics cultured with specialized microbes (Stavnes *et al.* 1996), oxygen-releasing sodium percarbonate (Vesper *et al.* 1994), and granular activated carbon (Davis-Hoover *et al.* 1999). All of those projects have been pilot tests involving one to several barriers that were created to evaluate the technology. The results from the tests are encouraging, suggesting that it should be feasible to use reactive barriers in source zones within the vadose zone, just as it is feasible to use them to degrade groundwater plumes downstream from those source zones. Nevertheless, the technology has not yet been applied at a full-scale nor has it been evaluated throughout the life of the reactive material. The technology is commercially available, but it has not yet been transferred beyond the original developers.

See case study "Case History of Reactive Barriers of Porous Ceramics Used to Enhance Biodegradation of Petroleum Hydrocarbons" by A. Yorke and T. Meiggs on page 1216.



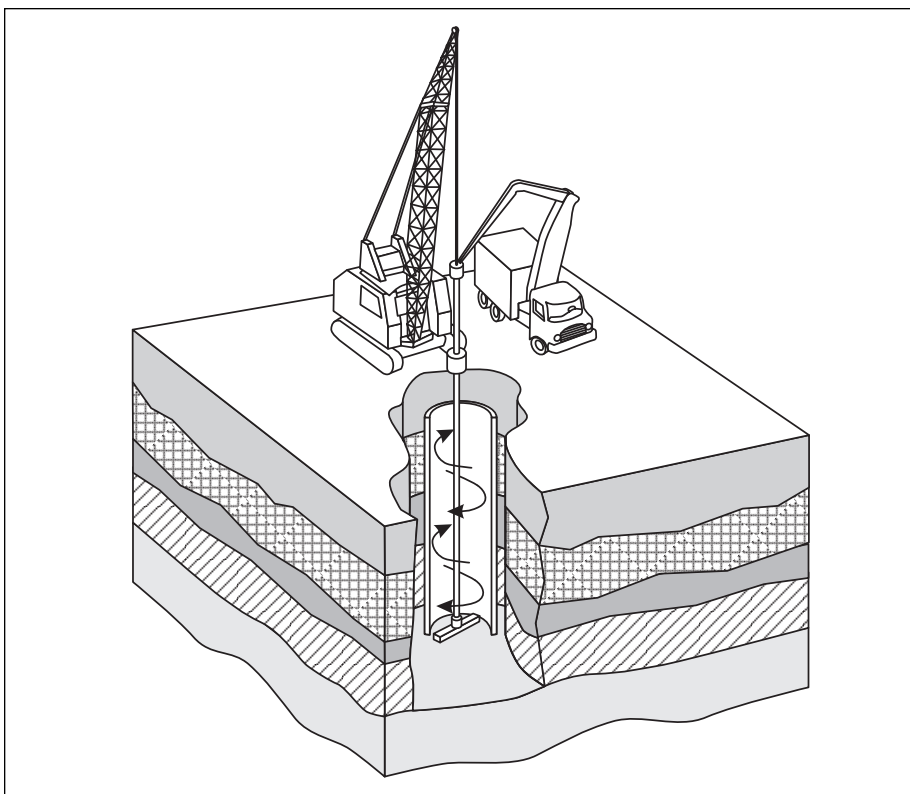
## DEEP SOIL MIXING: RECOVERY AND DESTRUCTION PROCESSES\*

*In situ* remediation can be exceedingly slow or of limited efficiency due to adverse properties of the subsurface, such as high organic matter content, low permeability, or contaminants with low vapor pressures, high K<sub>oc</sub>, or the presence of residual NAPL. A potential approach to rapid *in situ* treatment involves the use of deep soil mixing coupled with various physical or chemical treatment processes. In concept, soil mixing creates continuously mixed subsurface soil reactors where various treatment processes can be implemented (Figure 7-29). Vapor stripping, chemical oxidation and reduction, bioremediation, and solidification/stabilization processes have been evaluated under laboratory, and in some cases, field conditions (Table 7-10) (West *et al.* 1995a; Siegrist *et al.* 1995a,b; Gierke *et al.* 1995; DOE 1996; Cline *et al.* 1997).

This section describes *in situ* soil mixing treatment technologies coupled with either vapor stripping or chemical oxidation. Mixed region vapor stripping (MRVS) couples soil mixing with high pressure air injection and is potentially applicable at sites where contaminants are

---

\*This section was contributed by R.L. Siegrist and O.R. West.



**Figure 7-29.** Subsurface soil reactor using mixed-region processes for *in situ* treatment.

relatively volatile (West *et al.* 1995a; Siegrist *et al.* 1995a; Gierke *et al.* 1995; DOE 1996). Mixed region chemical oxidation (MRCO) combines soil mixing with *in situ* chemical oxidation and is potentially applicable to sites with oxidizable target compounds, such as petrochemicals and chlorinated solvents. This section presents a general description of soil mixing technology first. Descriptions of vapor stripping and chemical oxidation processes coupled with soil mixing as the delivery system follow, with process, principles, and experience.

## Principles

Soil mixing has evolved from construction drilling technologies to an approach for enabling remediation of contaminated sites by various *in*

**TABLE 7-10** Possible mixed-region processes.

Mixed-Region Processes	References
Vapor stripping with air, hot air, and/or steam (volatile organics)	U.S. EPA 1989; Roy 1990; West <i>et al.</i> 1995a; Siegrist <i>et al.</i> 1995a; DOE 1996; Cline <i>et al.</i> 1997
Flushing with surfactants, acids, chelating agents (organics and metals)	
Chemical oxidation with peroxide or permanganate (organics, metals)	Siegrist <i>et al.</i> 1995a; DOE 1996; Cline <i>et al.</i> 1997
Chemical reduction with zero valent iron metal (organics, inorganics, metals)	
Biodegradation with bioaugmentation (organics)	
Solidification/stabilization by grout injection (organics, metals, radionuclides)	Stinson and Sawyer 1989; Siegrist <i>et al.</i> 1995(b)

*situ* processes. Soil mixing can be used to accomplish several treatment objectives including: (1) recovery by stripping or flushing, (2) *in situ* destruction by chemical or biological methods, or (3) *in situ* immobilization by solidification/stabilization. Soil mixing enables rapid and extensive treatment in the vadose zone by subsurface disruption and facilitation of treatment agent contact and mass transfer. Mixing does not fully homogenize a subsurface region, yielding limited soil and contaminant translocation inward and upward within the mixed region. In concept, continuously mixed subsurface soil reactors can be created in various soils and sediments, including the vadose and saturated zones.

MRVS involves injection of compressed gases at high volumetric flow rates, such as 1 soil reactor volume per minute, to volatilize and advectively remove organic chemicals from the subsurface. The removed chemicals are either released to the atmosphere or captured in a shroud or hood and managed by a variety of offgas treatment techniques such as carbon adsorption or catalytic oxidation. MRVS utilizes various auger designs. Gas injection is accomplished through orifices

along the auger blade(s) or out the bottom end of a mixing shaft. Removal efficiency is dependent on contaminant and media properties, such as pore size and continuity, water content, and sorption, as well as injected gas properties like flow rate and energy content (West *et al.* 1993a; West *et al.* 1995a; Siegrist *et al.* 1995a; Gierke *et al.* 1995).

MRVS treatment time is a function of several factors, including: (1) the chemical properties (for example, vapor pressure and Henry's constant) of the target contaminants, (2) the partitioning behavior within the contaminant/media system ( $K_d$ ), (3) the physical properties of mixed soil/media, such as aggregate size and surface area, (4) the volume of soil to be treated, (5) the air flow rate and energy content, and (6) the required removal efficiency.

Laboratory and field tests of MRVS have shown that from 400 to 700 unit volumes of air (ambient temperature) per unit volume of soil (reactor volume, or *r.v.*) were required to reduce TCE concentrations in clay soils by at least 80 percent (West *et al.* 1995a). The treatment time for ambient air MRVS of a given mixed volume can be roughly estimated for a prescribed airflow rate. For example, for a treatment volume of 460 cu. ft (nearly equal to 6 ft diameter, 20 ft depth) and an air flow rate of 1,500 cfm, an estimated treatment time is obtained as follows:

$$\text{treatment time} = 400r.v. \times \frac{460 \text{ cu.ft.}}{1500 \text{ cfm}} = 123 \text{ min.} \quad (7.26)$$

This estimation procedure is thought to be valid for contaminants with vapor pressures similar to TCE, and for contaminant/soil systems that exhibit partitioning behavior similar to that of the TCE/soil system ( $K_d \approx 0.1 \text{ mL/g}$ ) studied by Siegrist *et al.* (1995a). For other contaminants, like gasoline or diesel, and other high organic content soil systems, laboratory tests and/or modeling, coupled with laboratory measurement, will be necessary to estimate required treatment times (West *et al.* 1995a; Gierke *et al.* 1995).

MRVS may enable secondary treatment through biological degradation in much the same manner that bioventing can during conventional SVE. This possibility was considered during a MRVS demonstration at a land treatment site in Ohio (Siegrist *et al.* 1995a). Comparisons of microbial activity before and after treatment revealed increases in total bacterial populations, (for example 1,000x) although the significance of this was not elucidated.

MRCO involves soil mixing that delivers an oxidizing agent to a subsurface region to achieve *in situ* destruction of organic contaminants. MRCO has been most commonly implemented with hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and potassium permanganate ( $\text{KMnO}_4$ ) oxidants (Table 7-11). However, other oxidants can be used, like ozone. Reductants are also feasible, such as zero-valent iron metal. (The principles and practices of chemical oxidation are discussed elsewhere in this chapter and are thus not described in detail here.) Depending on system pH, degradation of target organic chemicals and other reduced substances can occur by direct electron transfer or free radical processes (Siegrist *et al.* 1999). Since the reaction rates for most susceptible organic compounds are extremely fast, that is, in minutes, transport and distribution often control treatment efficiency and extent, assuming adequate oxidant is delivered to satisfy the demand of the target organic chemicals as well as natural organic matter and other reduced substances. Treatment efficiency appears to be a principal function of media properties, as in natural soil organic matter content and pH, oxidant concentration and mass loading rate, and uniformity of delivery and distribution. Oxidant solutions ( $\text{H}_2\text{O}_2$  at 0.01-10 wt. percent or  $\text{KMnO}_4$  at 1.0 to 4.0 wt. percent) have been mixed with contaminated soil to provide mass loadings that are 1,000 times greater than the stoichiometric requirements for degradation. The oxidant solutions are typically combined with soil at a ratio of 5 to 10 percent by volume (liquid volume per volume of treated media), which provides enough volume to disperse the oxidant without creating a slurry that produces free water. To enhance distribution of oxidant throughout the mixed region, hydrogen peroxide solution has been injected into an air stream, for example at 300 scfm, so that it enters the mixed region as a fine mist (Siegrist *et al.* 1995a; DOE 1996). In this approach, some organic compounds can be volatilized and advectively removed concurrently with the *in situ* oxidation processes. As in MRVS, any organic chemicals in the offgas are captured in a shroud covering the ground surface and managed by appropriate treatment techniques, for example, by carbon adsorption or catalytic oxidation.

### Implementation and Augmenting Technologies

Soil mixing was first used as an *in situ* remediation method in the late 1980s. The early applications were designed to deliver solidification



**TABLE 7-11****Example applications of *in situ* mixed-region processes for site remediation.**

<b>Location (date) Process</b>	<b>Media and COCs</b>	<b>Application method and results</b>
Florida (1988) <i>Solidification</i>	Sandy soil with PCBs to 5.5-m depth	EPA demonstration was completed at a PCB contaminated site in Florida where two, 10-ft by 20-ft areas were treated with cement-based solidification grout in 3-ft diameter columns to depths of 14 and 18 ft.
California (1989) <i>Steam stripping</i>	Soil with VOCs and SVOCs	At the San Pedro site over 8,000 yd <sup>3</sup> of soil was contaminated with up to 12,000 ppm of chlorinated hydrocarbons plus other volatiles and semi-volatiles from a few ppm to 50,000 ppm. Up to 99% removal of volatiles from the soil was achieved (efficiencies of removal ranged from 54% to 99+%). Semi-volatile organics (SVOCs) were removed with efficiencies ranging from 7% to 98%. Post-treatment concentrations of VOCs averaged 57, 53, and 71 ppm, respectively, in the three tests. For the SVOCs, 920 and 490 ppm remained after completion of two of the tests.
California (1989) <i>Steam stripping</i>	Soil with TPH to 6.1-m depth	At the Carson site, when the total petroleum hydrocarbon (TPH) concentration was less than or equal to about 1,000 ppm, removal efficiencies were 75 to 90% for a 15-ft deep soil column, with an average treatment time of 47 min. per column. When TPH was greater than 10,000 ppm, removal efficiencies were 90 to 95% in a 20-ft deep column, with an average treatment time of 78 min./column.
Ohio (1993) <i>Ambient and hot air stripping, Peroxide oxidation, and Solidification</i>	Silty clay soil with TCE and VOCs to	Comparative demonstration of soil mixing coupled with ambient (20°C) and hot air (120°C) stripping, chemical oxidation, or solidification to treat TCE and other halocarbons at 100 to 500 mg/kg. Use of a single 3-m augur to treat 3 overlapping columns to 4.6-m depth. Treatment time of 225 min yielded an average VOC removal efficiency of nearly equal to 92% for ambient air and nearly equal to 98% for heated air, while MRVS to 6.7-m depth with heated air was lower at approximately 88%. H <sub>2</sub> O <sub>2</sub> + compressed air injected during deep soil mixing to 15 ft depth in 3 10-ft diam. mixing zones. Up to 100 mg/kg mass reduced by 70% including 50% due to oxidation.
Kansas (1996) <i>Permanganate oxidation</i>	TCE and DCE in soil and ground water to 14.3-m depth.	Comparative demonstration of permanganate oxidation, bioaugmentation, and vapor stripping. KMnO <sub>4</sub> (3.1 to 4.9 wt.%) delivered by deep soil mixing (8 ft augers) to 47 ft bgs during 4 days. TCE reduced from 800 mg/kg by 82% in the vadose zone and 69% in the saturated zone (greater than 8 ft bgs). MnO <sub>4</sub> <sup>-</sup> depleted. Microbes persisted. Comparison tests with mixed region vapor stripping yielded 69% reduction with bioaugmentation yielding 38% reduction.

agents into the subsurface to immobilize contaminants such as PCBs (Table 7-11). During this same period, mixed region steam stripping emerged, and was evaluated at two sites in California (Treweek and Wogec 1988; Roy 1990). Three tests were conducted at a site in San Pedro, and the fourth was conducted at a petroleum-hydrocarbon-contaminated site in Carson. At that time, mixed-region processes involving ambient and hot air stripping as well as peroxide chemical oxidation and grout solidification were tested in Ohio (Siegrist *et al.* 1995a,b; DOE 1996). Later, permanganate chemical oxidation along with MRVS and bioaugmentation were evaluated during a field demonstration at a DOE site in Kansas City (Cline *et al.* 1997).

Today, implementation involves consideration of site conditions with respect to soil mixing technology (like depth and areal extent of contamination), site access and surface topography, surface or subsurface obstructions, and post-treatment land use, as well as treatment process chemistry and function (for example, soil texture and permeability, water and organic matter content, pH, type of contamination and treatment goals to be achieved). Implementation typically involves a series of activities from initial screening for site suitability and development of performance goals for the site, to development of a conceptual design. Site characterization data is gathered and used to verify design conditions. Laboratory bench-scale tests are recommended to verify or refine design parameters and document performance for a treatment process such as chemical oxidation. However, field-scale implementation remains uncertain until a field pilot-test is performed. This pilot-test can be performed before mobilizing to the field for a full-scale application, or as a shakedown test at the beginning of a full-scale application.

While soil mixing augments the implemented treatment process, there are other enhancements that might improve effectiveness. Thermophysical enhancements such as soil heating within low permeability deposits could enhance removal rates in some settings. Incorporating secondary treatment processes could also provide benefits. For example, passive volatilization and/or bioremediation enhancements could be implemented following MRVS or MRCO. Also, vegetative restoration techniques could be beneficially implemented following these processes. Finally, coupling could be envisioned for treatment of sites with mixtures of organic and metal contaminants, for example, MRVS followed by solidification/stabilization.

The cost and commercial availability of MRVS and MRCO technologies can be illustrated by considering a hypothetical site, 100 ft by 100 ft by 15 ft deep (nearly equal to 5,550 yd<sup>3</sup>). This site is characterized by stratified fine-grained media contaminated with gasoline that is diffused into the low permeability matrix blocks at a concentration of 1,000 mg/kg. The goal is to remediate the site to 200 mg/kg or lower. Based on full-scale data with chlorinated solvents like TCE, the estimated cost for MRVS (ambient or heated air) to achieve an 80 percent removal efficiency is approximately \$100-150/yd<sup>3</sup>; the cost for MRCO to achieve a 70 percent reduction is approximately the same. These costs are similar, because major costs are associated with mobilization/demobilization and mixing equipment operation. Coupling chemical oxidation with secondary processes might reduce the treatment costs. These data are projected based on a treatment cost of \$200/yd<sup>3</sup> treatment of TCE, as determined during a full-scale field demonstration at a secured DOE site where higher costs are normally encountered (Siegrist *et al.* 1995a). This assumes that off-gas treatment constraints are nominal. The estimated treatment time for the site is 30 to 60 days based on a processing rate of 100-200 yd<sup>3</sup>/d (Siegrist *et al.* 1995a; DOE 1996). Both MRVS and MRCO are commercially available technologies.

The case study "Mixed Region Vapor Stripping in a Silty Clay Vadose Zone," by R.L. Siegrist and O.R. West, describes an MRVS field test at the DOE's Portsmouth Plant in Piketon, Ohio. See page 1224.



### Critical Factors Affecting Performance

The soil mixing delivery system and the treatment process to be implemented, such as vapor stripping and chemical oxidation, are some of the critical factors affecting performance. There are many soil mixing factors to consider. Surface topography must be generally level (or be made so by grading) to provide a stable base for the mixing equipment. Surface obstructions such as parking lots, buildings, or overhead power or steam lines can limit access totally or make it exceedingly expensive. Subsurface obstructions such as buried utilities, boulders or rock, or construction debris can similarly limit application. The technique is unsuitable where contaminants occur in rock that cannot be disrupted

with an auger. Depth and areal extent of contamination are important, and, to date, most field applications have been accomplished at depths less than 16 m (50 ft), and in areas smaller than 1 hectare. Planned land use following mixed region treatment is very important because mixing causes a volume expansion of roughly 15 percent ( $1.5 \text{ m}^3$  within an above ground berm per  $10 \text{ m}^3$  of media treated *in situ*). This means that the height of the ground surface will increase during mixing, and the use of the land must be able to accommodate this change. (Siegrist *et al.* 1995a).

Critical factors related to treatment processes vary with each process. For MRVS, target chemical vapor pressure,  $K_{oc}$ , and contaminant concentration are important. With lower vapor pressures, high  $K_{oc}$ 's and high contaminant levels, benefits can be gained by using heated air, and even steam, rather than simply ambient air. For MRCO, critical factors include the target organic compound and whether it is amenable to oxidative destruction by peroxide or permanganate. Many organic chemicals are amenable to oxidative destruction but some are more susceptible to peroxide or Fenton's reagent compared to permanganate (Siegrist *et al.* 1999). Soil system pH and natural organic matter content are also important. Low pH, for example a pH of 4 to 5, and low NOM, for example less than 0.5 percent by weight, are generally preferred. It is also important to clarify the presence of metal co-contaminants that might be mobilized by redox effects.

## Monitoring

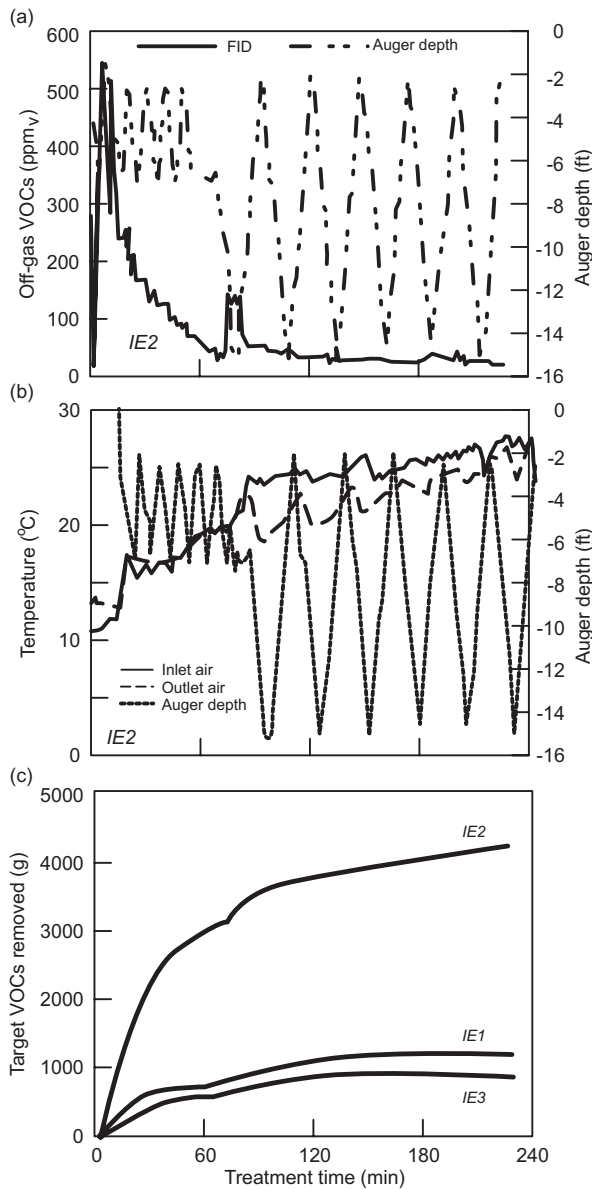
Several systems are used to monitor the MRVS processes. A sensor on the auguring tool can monitor auger depth. Offgas air flow rate and VOC concentrations can be monitored via flow meters and sampling ports in the shroud covering the mixed region. These measurements should be linked to the auguring depth record to enable interpretation of treatment progress. Offgas pressure and temperature provide insight into the operation of the system. These data can be readily tracked by sensors and recorded by a computerized data acquisition system (DAS) at intervals of approximately 0.5 to 3.0 minutes. In addition to this DAS sensor data, soil solid and soil gas samples can be collected before and after *in situ* treatment for analyses of physical, chemical, and biological properties. The treatment performance, such as total mass recovered and

residual organic concentrations, can be determined from the results of soil VOC analyses before and after MRVS (Figure 7-30) (Siegrist *et al.* 1995a; West *et al.* 1995b). The pre- and post-treatment data can be analyzed using statistical procedures employing classical descriptive statistics as well as stochastic simulation methods (West *et al.* 1995b). The estimated mass reduction calculated from soil concentration data can be compared to that calculated from the cumulative mass recovered in the offgas. MRCO is more difficult to monitor since chemical reactions occur within the mixed region during active mixing and reagent delivery, as well as during a period following cessation of mixing. Most of the above monitoring methods described for MRVS can also be employed for MRCO. In addition, analyses include reaction products, such as chlorides produced during oxidation of TCE.

### Status

It is possible to identify relative advantages and disadvantages of the MRVS and MRCO systems, although the state of knowledge and practice is currently insufficient to give firm guidelines for selecting these processes in a given setting. MRVS has the advantage of providing high treatment efficiencies while being simpler and easier to implement. Because chemical solutions are not involved in MRVS, chemical handling equipment is not required, injection permits are unnecessary, and health and safety hazards decrease. Moreover, since MRVS physically removes organic contaminants from the subsurface, online process monitoring and control is feasible. Finally, since no liquids are introduced, there is no potential for contaminant leaching. In contrast, MRCO has the advantage of more rapid treatment of not only volatile but also semi-volatile organic compounds. The addition of hydrogen peroxide yields oxygen, thereby enhancing potential biodegradation of original or partially oxidized organic compounds. MRCO also may enhance mixing efficiency and reduce mixing energy requirements. Finally, MRCO may reduce the potential for post-treatment leaching of untreated contaminants, for example, of heavy metals, by reducing matrix and bulk deposit permeability as a result of increasing water content and site compaction.

This mixed region strategy is an aggressive approach to *in situ* treatment and is most appropriate for source areas characterized by either high contaminant concentrations, biorefractory compounds, and/or sites



**Figure 7-30.** Results of MRVS using ambient air including (a) offgas VOC concentration, (b) offgas temperature, and (c) offgas VOC mass removal versus treatment time (Siegrist *et al.* 1995a).

with lower permeability media. Application to NAPL-contaminated low-permeability media is very attractive since it may offer the only way to rapidly and extensively disperse treatment agents and concomitantly remove/degrade contaminants in such settings. Much of the complexity and cost of a mixed-region treatment process (either MRVS or MRCO) is associated with mobilization/demobilization and operation of the soil mixing and delivery system. The costs associated with the treatment agents themselves, such as ambient air, heated air, and hydrogen peroxide, are relatively minor (less than 15 percent). Offgas treatment costs can represent minor or moderate costs, depending on the type and mass of contaminants, and treatment required.

The benefits of using heat (heated air or steam) in the MRVS process depend on the contamination properties; for example, concentration and solubility, and media properties like sorption and heat transfer. Benefits gained by injecting heated air are measurable and probably warranted for contaminant/media systems with relatively higher sorptive properties ( $K_d > 0.1$  mL/g). Injection of steam is more uncertain, as it may result in saturation and water flooding prior to system drying and vapor stripping of NAPL.

There is potential for coupling MRVS with MRCO and other complementary technologies like fracturing systems and oxidation, and bioremediation. For example, MRVS could be employed to remove the accessible volatile fractions followed by MRCO to facilitate degradation of the remaining less volatile or entrapped organic chemicals.

### **IMMOBILIZING ORGANIC CONTAMINANTS BY STABILIZATION AND SOLIDIFICATION\***

Solidification/stabilization (S/S) processes are among the most widely used methods for treating contaminated soils and waste materials in the United States today (U.S. EPA 1994). These processes have been used to remediate organic chemicals, but their primary application over the past 20 years has been to immobilize metals and other inorganic compounds in industrial sludges, contaminated soils, fossil-fuel fly ash, incinerator residues, and other hazardous wastes. The U.S. EPA now

---

\*This section was contributed by P. Bishop and V. Hebatpuria.

recognizes S/S technology as an acceptable method for treating materials with metal contamination (U.S. EPA 1989), and the technology is used more often than any other hazardous waste management alternative. However, the ability of S/S methods to treat organic contaminants is more controversial.

Land-ban regulations (Anon 1985) prohibit disposal of hazardous liquids in landfills and require that the wastes be solidified, with a minimum of free water, before landfilling. This can be accomplished by S/S processes. Stabilization refers to techniques that reduce the hazard potential of a waste by converting the contaminants into their least soluble, mobile, or toxic form. The physical nature and handling characteristics of the waste are not necessarily changed by stabilization. On the other hand, solidification refers to techniques that encapsulate the waste in a monolithic solid of high structural integrity. It does not necessarily involve a chemical interaction between the waste and the solidifying reagents, but may mechanically bind the waste into the monolith (Conner *et al.* 1990). Together the S/S processes can transform liquid wastes so that they meet the requirements of land-ban regulations, allowing those wastes to be placed in landfills.

The most common S/S processes use Portland cement, lime/fly ash, or other pozzolanic materials as a binder for stabilizing contaminants into a relatively immobile form and solidifying them into a rigid mass. Cement-based techniques can cost-effectively stabilize heavy metals in sludges and soils. Unfortunately, many of these waste materials also contain toxic organic chemicals, which may not be immobilized as effectively as heavy metals. A great deal is known about the chemical processes involved with stabilizing metals in cement, but relatively little is known about the mechanisms involved with the release, or leaching, of organic chemicals from stabilized waste. This section provides an overview of organic compound leaching from S/S contaminated soils, reviews what is currently being done to improve the immobilization of these compounds, and describes what new techniques are being developed. Applications for S/S on metal-bearing wastes are described in Chapter 8.

## Principles

Leaching from stabilized solids into water that percolates through the waste is the primary mechanism for release of contaminants to the envi-



ronment. As a result, the leaching rate is the major criterion for evaluating stabilized wastes (Conner *et al.* 1990). The leaching rate is typically estimated using one or more standardized laboratory tests, such as the Toxicity Characteristics Leaching Procedure (TCLP). A variety of such tests are available (Means *et al.* 1995) and most of them involve placing samples of the stabilized material in containers of water or weak acid (to simulate acid rain). The containers are agitated and the concentrations of contaminants in the water are measured either after a specific time has elapsed, or at several times during the test. The leaching rate can be estimated by comparing the concentration of the contaminant that leached into the water during the test to some reference concentration, such as the drinking water standard. Alternatively, the leaching rate can be characterized by fitting concentrations measured as a function of time using a transport model.

In typical S/S systems, most metals precipitate as insoluble carbonates, silicates, sulfates, and other salts, in the highly alkaline environment created by reactions with Portland cement. These metals are encapsulated in the gel-like structure of the binder matrix. Those processes significantly reduce the leaching rate of most metals (Bishop 1988).

Organic chemicals show no such behavior. They rarely precipitate due to an increase in pH, and, typically they fail to bind to cement. Organic chemicals may be sorbed or encapsulated in pores in some cement material, but this stabilization effect is often short-lived. While there are a few examples where organic compounds can be hydrolyzed, oxidized, or reduced due to reaction with cement (Conner 1990; Lear and Conner 1992), such cases are uncommon. In most cases, organic chemicals are released relatively rapidly from conventional S/S material, although the release rate does depend to some degree on water solubility, polarity, presence of functional groups, and volatility (U.S. EPA 1993). Most experts consider conventional S/S processes inappropriate for long-term containment of organic chemicals at moderate-to-high concentrations. This is particularly true for volatile chemicals, but also for most semi-volatiles (Battelle 1993).

The need to improve the organic chemical immobilization in S/S material has motivated a great deal of research, most of which has focused on materials that strongly sorb organic chemicals before being added to cement. For sorbants to be effective, however, investigators had

to address an even more insidious problem: organic chemicals may actively interfere with chemical processes within the cement itself.

### **Interferences Caused By Organics**

Many organic chemicals may actually retard or accelerate the hydration of cement binders (Cartledge *et al.* 1990). This can reduce the strength of the solidified material, or it may prevent the cement from solidifying altogether (Cartledge *et al.* 1990; U.S. EPA 1993). Even low concentrations of organic chemicals in a mixed waste may reduce strength and interfere with hydration, (Pollard *et al.* 1990).

The interference effects are due to interactions at the molecular level. For example, Phenol is known to reduce the long-term strength of cement even at concentrations as low as 2000 mg/L (U.S. EPA 1993). Detailed examination shows that 3-chlorophenol inhibits cement hydration by stabilizing ettringite formation, retarding its conversion to monosulfate within the waste form (Montgomery 1989). Another microstructural study showed that methanol and phenol inhibited ettringite formation, but trichloroethylene appeared to stimulate it (El-Korchi *et al.* 1989). A potentially beneficial effect was observed with 1,3,5-trichlorobenzene, which decreased the pore diameters in the waste, causing entrapment and reduced leaching of the contaminant (Riaz and Zamorani 1989). Ethylene glycol, p-bromophenol, and p-chlorophenol also interact with cement (Tittlebaum *et al.* 1986). Ethylene glycol can inhibit hydration by occupying three distinct sites in the hydrated cement matrix, and can also alter the cement microstructure, producing grainy nodular surfaces that lack crystallinity. The ethylene glycol molecule is apparently small enough to substitute for water during hydration, but it deforms the resulting structure in the process. Both p-bromophenol and p-chlorophenol interact with the calcium-silicate-hydrate gel that forms during the hydration of cement, although the details of the interaction are slightly different for the two compounds (Tittlebaum *et al.* 1986). The potential interactions between organic chemicals and cement-based S/S systems (U.S. EPA 1993) are summarized in Table 7-12.

**TABLE 7-12** Interference effects due to the presence of organics in S/S systems.

Compound	Potential Interference
Phenols	Decrease compressive strength for high phenol levels
Semi-volatile organics/PAHs	Interfere with bonding of waste materials
Polar organics (alcohols/ organic acids/glycols)	Impede setting of cement, decrease short-term and long-term durability. Alcohols may retard setting of pozzolans.
Solid organics (plastics, tars, resins)	Ineffective with urea formaldehyde polymers; may retard setting of other polymers.
Aliphatics hydrocarbons	Increase setting time for cement.
Chlorinated organics	Increase setting time and decrease durability of cement if concentration is high.
Non-polar organics (oil/ grease/PCBs)	Impede setting of cement, decrease long-term durability and allow escape of volatiles during mixing

### Adsorbent

Adsorbents, which show promise as a material for organic chemical stabilization, have been used by the S/S industry for many years (Conner 1995), but most are proprietary and relatively expensive. The research community is investigating a variety of relatively inexpensive materials, including activated carbon, quarternary ammonium-exchanged clays (organophilic clays, or organoclays) and zeolites that could be used to absorb organic chemicals in wastes prior to cement-based solidification. In one study, fly ash, bentonite, virgin activated carbon, and soluble silicates were used to absorb various organic compounds (Caldwell *et al.* 1990). Activated carbon was the most effective of the sorbants tested. The insoluble, non-volatile compounds tested in this study were tightly bound in the S/S matrix. The distribution coefficient decreased and the leaching rate increased as solubility and volatility of the contaminants increased; however, volatile contaminants were poorly immobilized by the sorbants.

Several studies have identified activated charcoal as an important sorbant. Kyles *et al.* (1987) screened a range of conventional and novel processes for S/S of four wastes, including electroplating filter cakes

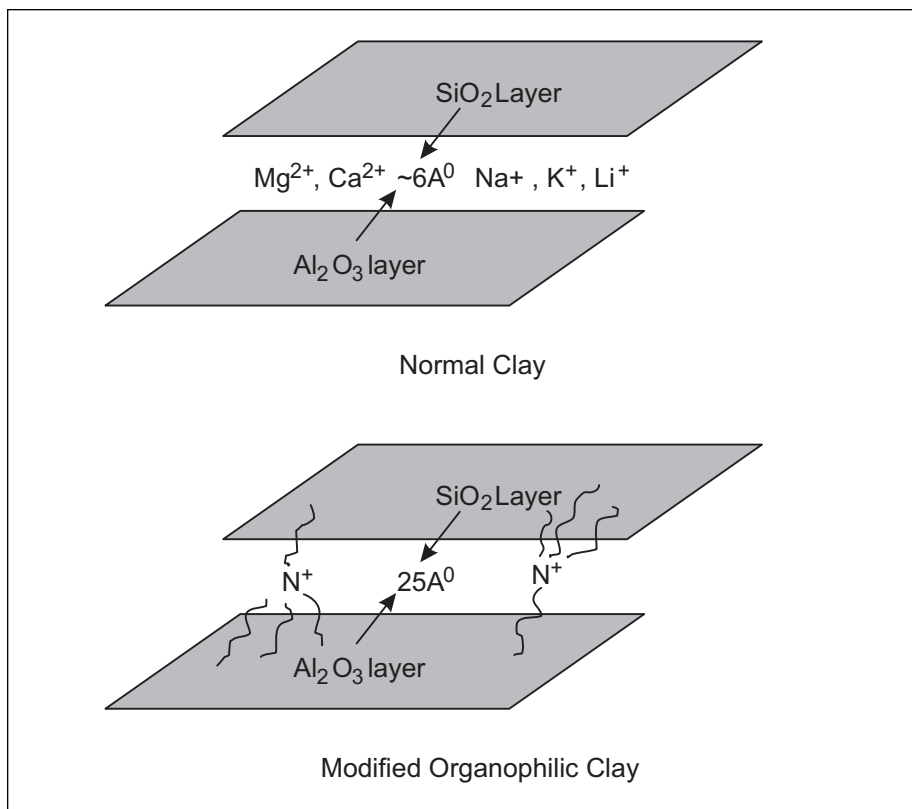
contaminated with chlorinated organics, a mixed waste containing dyes and pigments, an oil filter cake, and an acidic tar residue. The adsorbents used in the study were kiln dust, calcium oxide, and activated carbon. The study shows that activated carbon was the only compound to effectively immobilize the organic constituents. Sheriff *et al.* (1989) used decolorizing charcoal and quarternary-ammonium-exchanged clay for the cement-based fixation of 3-chlorophenol and 2,3-dichlorophenol (100 to 2000 mg/L). The charcoal rapidly adsorbed the contaminants and immobilized them in the S/S waste matrix, and the charcoal appeared to aid cement hydration and increase compressive strength. Another investigation showed that several materials could adsorb as much as 30 percent (w/w) of an oily waste and then be successfully solidified in ordinary Portland cement (Lin and Mackenzie 1983).

### Modified Clays

Normally hydrophilic clay minerals can be modified to increase their capacity to adsorb organic chemicals. One method for creating organophilic clays is to substitute quarternary ammonium compounds for cations between the silica and alumina layers in the mineral structure of montmorillonite, the major clay mineral in bentonite. The quarternary ammonium compounds contain long-chain alkyl or aromatic groups that make the space within the clay less polar and more hydrophobic, increasing the attraction of the clay for many toxic organic compounds (Figure 7-31).

Organophilic clays composed of bentonite containing tetra-alkylammonium compounds were used to adsorb various phenols before being incorporated into the cementitious matrices in several studies (Montgomery *et al.* 1991a; Montgomery *et al.* 1991b; Sheriff *et al.* 1989; Mortland *et al.* 1986). The partitioning coefficients of the modified clay increased with the degree of polarity and the addition of chlorine; that is, the partitioning of phenol < chlorophenol < dichlorophenol < trichlorophenol.

Thermally treated but unexchanged clays have also been utilized for adsorption of organic chemicals. Escher and Newton (1985) used a mix of Portland cement and bentonite clay to solidify wastes contaminated with cyanide and phenol. In another study, spent clay from the edible oil industry was modified to a low-cost clay-carbon adsorbent by the chemical activation of residual oil on the mineral surface. Activated



**Figure 7-31.** Modifying a clay with a quaternary ammonium compound.

bleaching earth was also evaluated for the cement-based S/S of an organically contaminated pickling acid waste, and its performance was compared with that of activated carbon used in drinking water treatment (Pollard *et al.* 1990). Adding 10 percent (w/w) of the modified clay reduced the leachable total organic carbon (TOC) by as much as 37 percent (w/w). Also, the pozzolanic activity of the clay increased the compressive strength of the waste by 2 to 3 times.

### Fly Ash

Fly ash is one of several materials (including blast furnace slag and cement kiln dust) produced as an industrial byproduct that will react

with lime to form a pozzolanic cement. Many researchers (Davidson *et al.* 1958; Leonard and Davidson 1959; Thorne and Watt 1965) have proposed that reactive sites of fly ash will sorb unpyrolyzed organic compounds and prevent interaction with cementation reactions. Soils contaminated with PCBs were solidified by a commercial S/S process using fly ash and additives (Myers and Zappa 1987). The process produced negligible volatile and leachable TOC in leach test filtrates, but details of this proprietary process were not disclosed.

Pozzolans have been shown to solidify clay soil contaminated with simple alcohols and substituted aromatics with an organic content of 11.4 percent (w/w) (Thornton *et al.* 1975). The addition of 5 percent (w/w) lignite fly ash increased the compressive strength by 40 percent. Investigations of cement strength showed that aliphatic and dicarboxylic acids neutralized lime, and, therefore, interfered with pozzolanic hydration (Smith 1979).

### **Proprietary Additives**

Many companies sell proprietary additives, which they claim, will effectively immobilize toxic organics in S/S matrices. It is often difficult to substantiate these claims because the stabilization ingredients are kept secret and leaching tests are generally only performed by the vendor. However, one validated study was performed in which two additives (KAX-50<sup>™</sup> and KAX-100<sup>™</sup>) containing rubber particles were compared with activated carbon, an organophilic clay, and untreated contaminated soil (Conner 1995). The two proprietary additives were found to be superior for stabilizing most of the organics tested, though the high cost of these additives may make their use uneconomical in many cases.

### **Activated Carbon**

Activated carbon appears to be the most effective adsorbent in immobilizing organic contaminants in soils (Caldwell *et al.* 1990). However, virgin activated carbon is too expensive to use during large-scale S/S processes (Conner 1990). One way to realize the benefits of activated carbon but reduce costs is to use thermally reactivated carbon. The demand for this previously used, but regenerated, carbon is generally low, making it relatively inexpensive (only about 20 to 25 percent of the cost of virgin activated carbon).

An extensive study of the use of reactivated carbon to immobilize organics in S/S systems is currently underway (Arafat *et al.* in press; Hebatpuria 1998; Hebatpuria *et al.* in press-a; Hebatpuria *et al.* in press-b). Preliminary results show that contaminated soils containing a wide range of volatile and semi-volatile organic compounds (for example phenol, aniline, naphthalene, and 2-chlorobenzene), can be effectively immobilized in a cement-based S/S process using thermally reactivated carbon as the preadsorbent (Figure 7-32). Only 0.5 to 2 percent (w/w) reactivated carbon was needed. Adsorption was very rapid (Figure 7-33), so premixing of the soil with the reactivated carbon was not needed; it could be added to the contaminated soil along with the cement. Moreover, immobilization of the organic chemicals appears to be essentially permanent; leaching studies using aggressive leachants failed to remove the organics from the S/S matrix even after much of the cement gel structure had been dissolved, an effect probably due to the cement sealing the micropores of the activated carbon, which contain much of the contaminant.

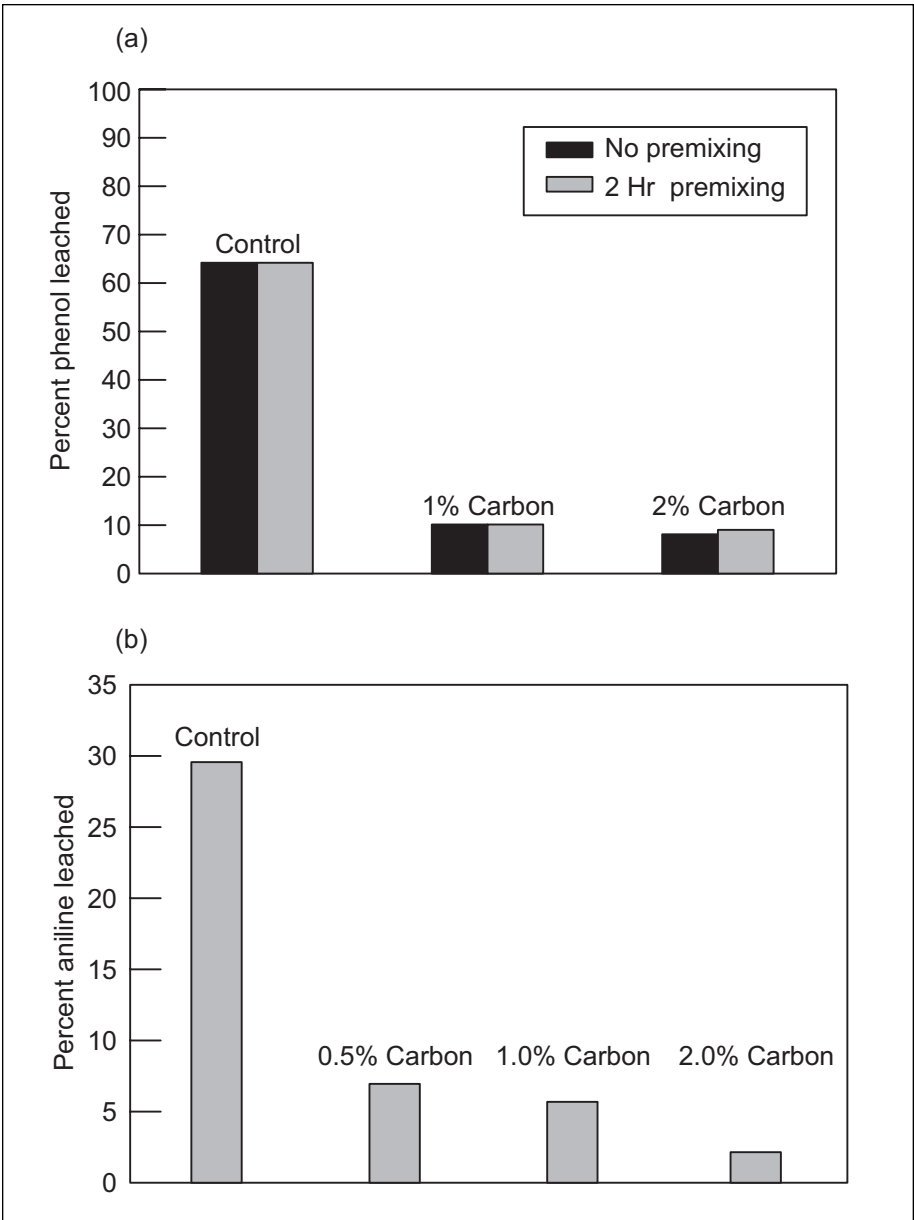
### Implementation

S/S processes can be used either *ex situ* or *in situ*. The *ex situ* process involves excavating contaminated soil and mixing it with suitable binders and additives (U.S. EPA 1993), and then placing this mixture into designated hazardous waste landfills. In most *ex situ* applications, the resultant slurry can be handled in several different ways: it may be (1) poured into containers or molds for curing followed by off-site disposal, (2) poured into cells or trenches for disposal onsite, (3) injected into the subsurface environment, or (4) reused as construction material, with appropriate regulatory approvals.

The *in situ* processes require the use of large augers, or similar devices, that can inject binder and mix it directly with the contaminated soil. *In situ* S/S processes can reduce costs by eliminating the need for excavation, but they can be less effective because of incomplete mixing. Figures 7-34 and 7-35 depict generic elements of typical *ex situ* and *in situ* processes (U.S. EPA 1993).

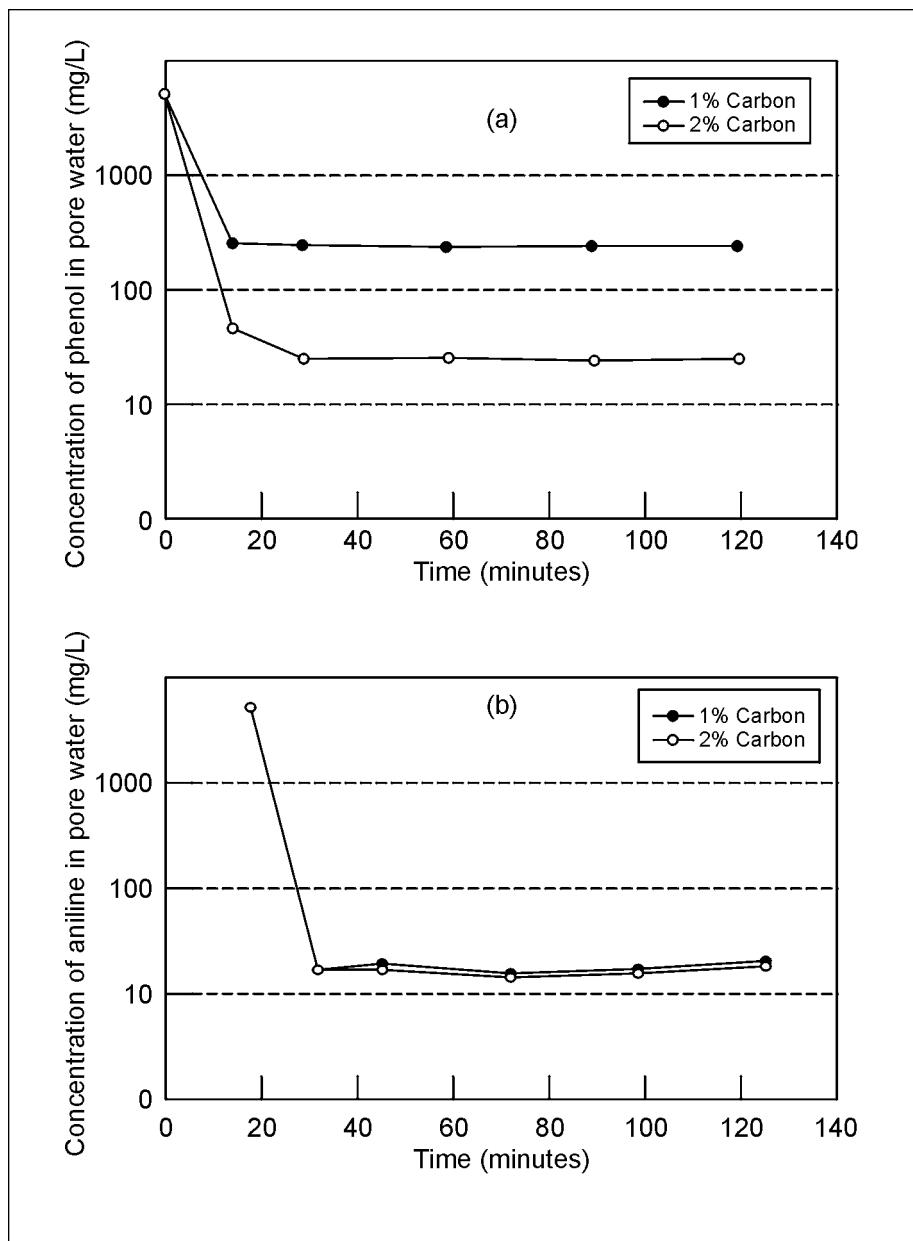
### Feasibility Screening

The U.S. EPA has developed an approach that determines the feasibility of S/S for treating organically contaminated soils (Means *et al.*

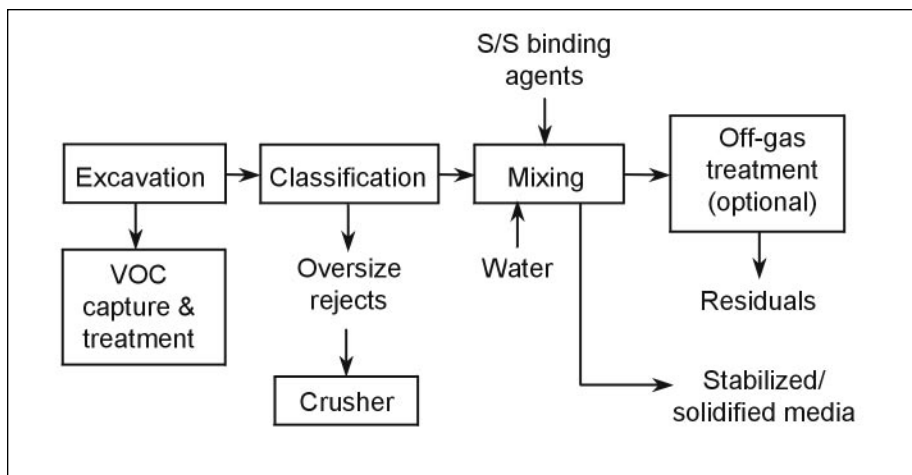


**Figure 7-32.** TCLP analyses of solidified/stabilized soils containing (a) phenol and (b) aniline using various carbon loadings. Specimens had a liquid:solids ratio of 10:1 and were cured for 7 days prior to testing.

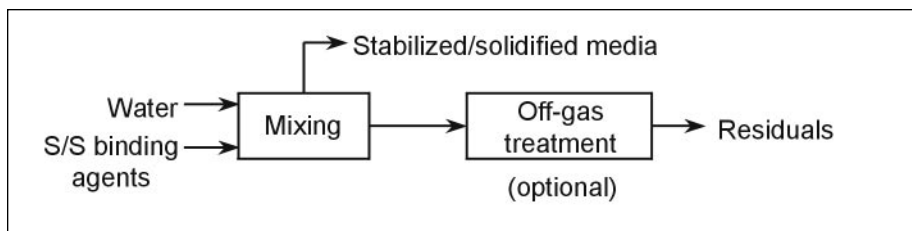




**Figure 7-33.** Time required for immobilization of contaminants using thermally reactivated carbon as the adsorbent.



**Figure 7-34.** Generic elements of typical *in situ* S/S process.

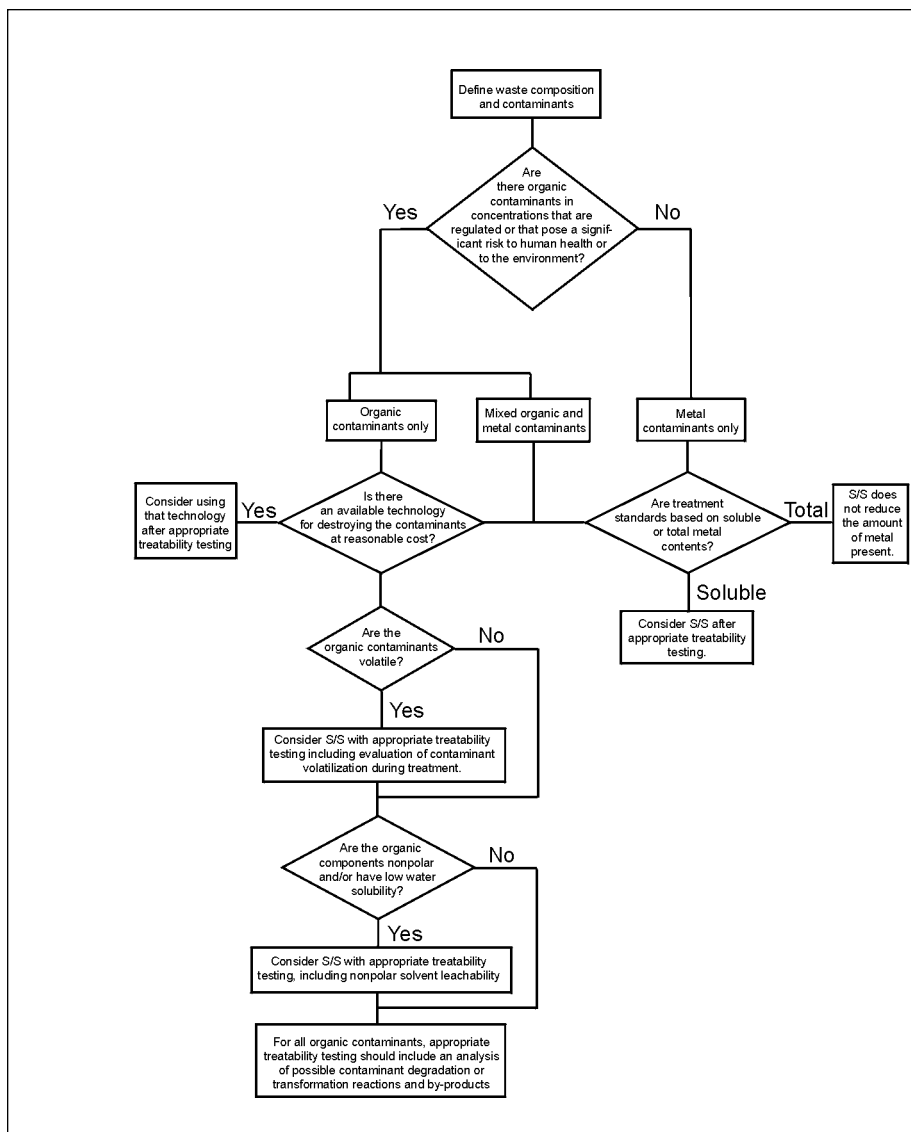


**Figure 7-35.** Generic elements of typical *ex situ* S/S process.

1995). The decision tree shown in Figure 7-36 is used to determine whether S/S technologies provide an acceptable alternative for treating a particular waste containing organics. This screening approach determines whether S/S treatment will destroy or remove the toxic organic components, release them to the air during treatment, or release them in solidified/stabilized waste leachate.

### Augmenting Technologies

Recovery technologies such as SVE can be used to reduce concentrations of organic chemicals before S/S processes are used. This



**Figure 7-36.** Decision tree for determining whether S/S technologies provide acceptable alternatives for treating particular organic waste.

preliminary step reduces potential interferences with organic chemicals and lessens the burden of preventing their mobilization. In some cases, *in situ* technologies can be used prior to stabilization, whereas in cases where S/S involves excavation, it may be feasible to pre-treat waste above ground to remove organic compounds. A two-step process of recovering or destroying organic contaminants and then using S/S to remediate metal contamination can be effective method for treating mixed waste.

### **Critical Factors Affecting Performance**

The major determinants governing the performance of S/S processes for soils contaminated with organic compounds are the types and amounts of organics present, the type of soil being treated, the volume of contaminated materials requiring treatment, and the depth to which the contamination in the soil extends.

Organic compounds with low volatility and low solubility in water are most suitable for incorporation into a S/S matrix. Highly volatile (and even many semi-volatile) organic compounds may be lost to the atmosphere during excavation, mixing, and subsequent processing of the soil. These problems may be overcome by *in situ* S/S, where binder chemicals and water are injected into the soil and mixed in place using soil augers. Highly water-soluble organics may only be encapsulated within the S/S matrix and may readily leach out later. S/S treatment may be unsuitable for these compounds, although the addition of an adsorbent such as activated carbon or organophilic clay may immobilize the organics in the waste form. Some organics are incompatible with cement binders, causing accelerated or delayed setting, or no setting at all. Adsorbents may be successful in trapping the organics and preventing them from interfering with the cement setting reactions, but this has not been fully investigated. These factors can be evaluated using bench-scale tests.

The type of soil to be treated is also important. Clayey and some silty soils can act as strong sorbents and help to hold organic contaminants in the S/S matrix. These soils could be good candidates for S/S treatment. Sandy soils fail to sorb many organic contaminants and may be less suitable for S/S treatment unless an adsorbent is added along with the binders. Highly organic soils may interfere with the cement setting reactions.

Large amounts of binder chemicals are needed to effectively stabilize and solidify contaminated soils. Thus, the cost for processing large vol-

umes of soil may be prohibitive. Another drawback to this treatment is the volume increase exhibited by the treated soil, which may have a final volume that is 10 to 40 percent greater than the original. If the S/S material is kept onsite, provision must be made for the increase in elevation accompanying the volume change; if it is hauled to another disposal site, the resulting increase in volume must be considered when selecting the site.

The depth of contamination is also important. There are limits to how deeply binder chemicals can be effectively injected and mixed into the soil. There are claims that this can be done to a depth of 30 m, but most feel that *in situ* stabilization should be limited to the upper 10 to 15 m. *Ex situ* S/S requires excavation of all soil material. Obviously, the deeper the contamination, the more costly the excavation and total treatment costs.

## Monitoring

Monitoring at S/S sites is often complex because the effectiveness of the process depends on chemical reactions that occur in the subsurface. Consequently, intensive testing to determine the treatability of the waste and proper mix formulations, and rigorous quality control and monitoring of the mixing process is needed. Commonly, with *ex situ* processing, the S/S waste is immediately placed back into the ground as an uncured slurry. Any problems with improper setting may go undetected. In a few instances, the waste form is placed in a mold after mixing and held until the waste sets, to insure that it is properly solidified, but this procedure is usually too expensive for large operations. Intermediate testing is typically impossible with *in situ* treatment. Here, the effectiveness of the soil mixing with the binders is of paramount importance, but reliable techniques for monitoring *in situ* mixing are currently unavailable. Once the soil has been treated and placed in the ground, the pore water in the solidified mass is also difficult to monitor. Typically, monitoring must be done at the perimeter of the site. Monitoring wells have been placed below the site, but they are uncommon.

## Status

S/S of heavy metal-contaminated soils is a mature, well-accepted process, used at many hazardous waste sites as the sole treatment

process, or in combination with other technologies. Approximately 40 percent of all Records of Decision include S/S as part of the treatment process. Many of these sites also contain toxic organic chemicals. In some cases, immobilization of the organics has been effective; in others it has been less so. Few sites whose primary objective is treatment of organics have used S/S because better technologies are available. The exceptions are sites that are contaminated with heavy, non-volatile, low-solubility organics, such as coal tars or petroleum residues. Here, S/S processing may be suitable because it is unlikely that the organics will readily leach from the solidified waste form.

## **PHYTOREMEDIATION\***

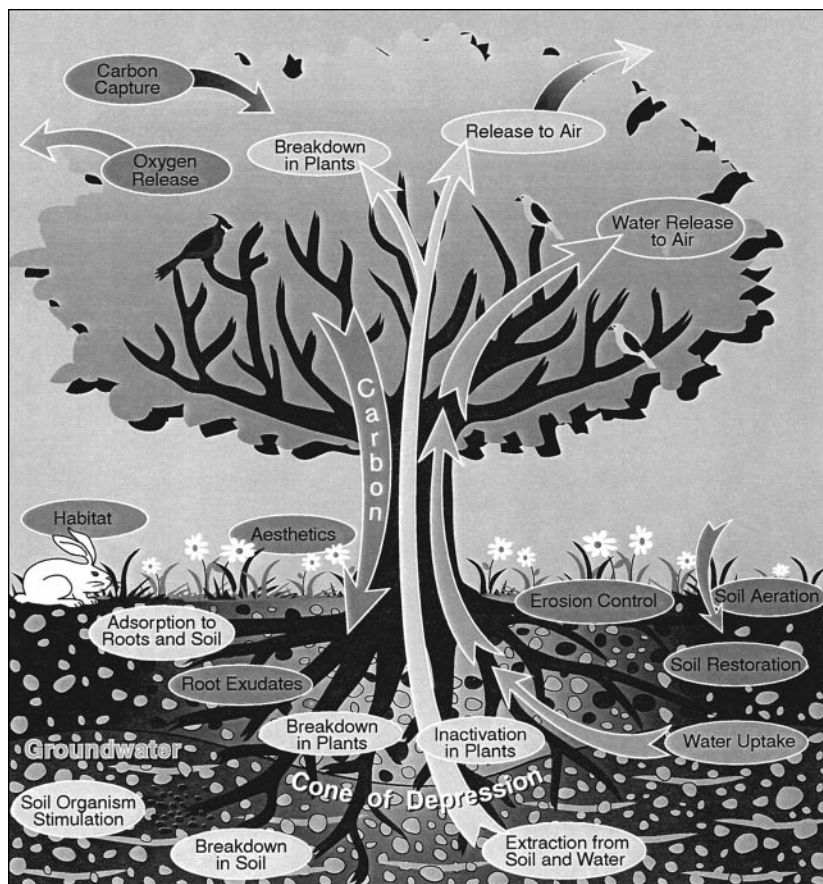
Natural processes accompanying plant growth affect the fate of organic contaminants in several ways (Fig. 7-37). Plants move water from the subsurface to the atmosphere, which transports vadose zone contaminants to the root zone (the rhizosphere), where microbes are usually concentrated. Organic compounds may be biodegraded by microorganisms in the rhizosphere, transported into the plants, and/or adsorbed to the organic matter associated with the vegetation. Some compounds are transformed, either in the plant or in the soil, to other organic forms that become part of the plants, microorganisms, or humic matter of the soil.

### **Principles**

Phytoremediation includes all processes where plants play a leading role in remediation; some of these processes involve microbes associated with plants. As a result, phytoremediation is closely linked with bioremediation, which is described earlier in this chapter. Many phytoremediation processes relate to the ability of plants to move water through the vadose zone by evapotranspiration. This pumping effect removes as much as 2 meters of water per year ( $2 \text{ m}^3/\text{m}^2/\text{yr}$ ). Evapotranspiration is significant as water and contaminants are moved to the root zone of the plants, where contaminants can be transformed by a

---

\*This section was contributed by L.E. Erickson, L.C. Davis, and P.A. Kulakow.



**Figure 37.** Processes involved during phytoremediation.

diverse microbial population in the rhizosphere. Some contaminants are transported into the roots and are transformed within the plants themselves. Volatile contaminants may be transported completely through the plant and released to the atmosphere either through leaves or through gas phase diffusion in the vadose zone.

Evapotranspiration reduces the amount of water in the subsurface and extends the depth of the vadose zone, allowing volatile contaminants to be released to the atmosphere and oxygen to diffuse to greater depths. Since many organic compounds are aerobically biodegraded, the gas phase diffusion of oxygen within the subsurface can significantly increase remediation.

Evapotranspiration can inhibit contaminants from moving below the root zone of plants. Since some plants have rooting depths of 10 meters or more, considerable moisture can be stored temporarily in the root zone. The soil moisture can range from field capacity to near wilting point conditions. Table 7-13 shows the estimated water storage capacity of several different soils. For example, a silt loam soil with 2-meter root depth can store 34 to 44 cm<sup>3</sup>/cm<sup>2</sup> of water. By combining the storage capacity of the soil with the pumping capacity of plants, a system is produced that limits the amount of precipitation extending past the root zone. This concept has been used to create vegetative caps that reduce infiltration and are less expensive than conventional caps used on landfills. Plants have also been placed near landfills and other contaminated sites to arrest the migration of plumes of contaminated groundwater. Plants can develop a cone of influence, similar to a well, such that shallow groundwater moves into the region where the vegetation is.

Plants contribute to the management of surface water at many contaminated sites. Vegetation reduces runoff and erosion, thereby limiting the movement of contaminants from the site in dissolved and suspended forms. In cases where plants are used to capture and evapotranspire precipitation, ensuring that there is surface runoff with appropriate treatment during periods of large amounts of rainfall will reduce the infiltration and enhance the probability of containing all of the infiltration in the root zone.

Complex processes involving microbes in the rhizosphere can destroy some organic contaminants. Microorganisms flourish in the root zone of many plants, where they are sustained by root exudates and organic mat-

TABLE 7-13

Approximate available water storage capacity of various soils based on differences between field capacity and wilting point. Data from various sources.

Textural Class	Estimated Storage Capacity, % Water
Silt loam	17-22
Loam	12-21
Silty clay	14-19
Sandy loam	4-16
Clay	11-15
Clay loam	5-10
Sand	2.5



ter from decaying roots (Table 7-14). The energetics of this process begin with solar radiation and can be quantitatively traced through the rhizosphere (Table 7-14). Microbes take advantage of the carbon and energy supplied by plants (Table 7-15). Microbial populations are often more than one order of magnitude larger near the root surface than they are elsewhere in the soil. The plant-supplied organic matter is a mixture of aliphatic and aromatic compounds, which either include or resemble compounds that are organic contaminants. Rhizosphere microbes often develop the capacity to degrade organic contaminants because similar compounds occur naturally in their environment. The degradation process is driven largely by microbial enzymes, but plant enzymes contribute as well.

**TABLE 7-14**

**Bioenergetics of plant growth and energy flow to the rhizosphere. Approximate values from Erickson *et al.* (1995). For these processes, energy flows of enthalpy and free energy are of similar magnitude. Root exudates can sustain about  $10^8$  cells/g soil.**

Process	Energy Flow
Solar energy transformed to:	
Chemical energy (0.7–3.2%)	1.5 kJ/kg soil day
Chemical energy in fixed carbon transported to root zone (30–50%)	0.45–0.75 kJ/kg soil day
Chemical energy supplied to soil as root exudates (40–70% of carbon flow to root zone)	0.18–0.52 kJ/kg soil day
Maintenance energy needed for aerobic vegetative cells	137 kJ/gmole microbial biomass carbon day or 1.6 nJ/cell day

**TABLE 7-15**

**Sources of organic carbon that contribute to the diversity of biodegradation capability in the rhizosphere.**

Root exudates including sugars, amino acids, organic acids, enzymes, and nucleotides  
Mucilages consisting of mainly polysaccharides and polyglacturonic acid  
Sloughed-off plant cells and their lysates  
Root hairs that die and decay  
Microbial cells that die and decay  
Plant leaves and stems that fall to the soil surface

Organic compounds can also be sorbed and immobilized by organic matter in the rhizosphere, reducing the bioavailability of contaminants and their associated health risks. Contaminants that desorb from the organic matter become available to potential degradation by microbes, although some contaminants may escape degradation and migrate out of the rhizosphere.

Organic contaminants can enter plants, move up into the stems, and be evaporated from leaves as a natural analog to the pump-and-treat process. Interestingly, the pumping system utilized by plants can remove water held by capillary forces in the vadose zone much more effectively than mechanical pumps developed by man. Because contaminants can be toxic to plants, however, the vadose pumping system that they have developed does have drawbacks. Many commonly occurring VOCs can be transported through plants and evaporated from their leaves without significantly crippling the plant. However, details of this process are only beginning to be recognized. Toxicity studies and monitoring the concentration of contaminants should be part of any phytoremediation project.

Mathematical models describing the movement of contaminants into and through plants have been developed and used to explain experimental results by a variety of investigators, including Trapp and McFarlane (1995), Burken and Schnoor (1998), and Davis *et al.* (1998a, b). The fates of compounds such as toluene and TCE have been modeled by Narayanan and others (Narayanan 1998; Narayanan *et al.* 1998a, b; Davis *et al.* 1998a, b; Narayanan *et al.* 1998a, b;), who show that toluene is biodegraded aerobically in the root zone, whereas TCE diffuses into the atmosphere. The effect of plants and root exudates on biodegradation of polynuclear aromatic hydrocarbons has been modeled and compared with experimental data by Santharam *et al.* (1994). Their research found that biodegradation in vegetated plots achieved lower concentrations than it did in unvegetated plots due to rhizospheric processes.

The case study "Phytoremediation of Petroleum Contaminated Soil," by L.E. Erickson, P.A. Kulakow, and L.C. Davis, describes several field studies of phytoremediation at sites contaminated with petroleum hydrocarbons. See page 1234.



## Implementation

Phytoremediation utilizes common agricultural and horticultural methods. In some applications, fertilizers are needed to provide nutrients for plant growth. Irrigation may also be provided if rainfall does not arrive when needed.

Details of the design of a particular implementation may vary considerably, depending on many factors including the following: (1) contaminant issues, such as biodegradability, bioavailability, plant toxicity, depth, and concentrations, (2) plant issues, such as properties of available native plants (root depth, evapotranspiration rate, potential degradation mechanism), climate, growing season, soil fertility, and (3) site issues, such as plume management objectives, future plans for the site, time for treatment, health risks to humans and animals during treatment, risk-based standards, and regulatory expectations and limits.

Poplar trees, cottonwood trees, and alfalfa are often used because of their high evapotranspiration rates. Since alfalfa fixes nitrogen, this crop has advantages where the contaminants or soil lacks nitrogen. Alfalfa can be planted inexpensively, and, in many cases, can be harvested and used as animal feed. Poplar and cottonwood trees can be planted as whips cut from growing trees. Trees should be planted in the spring while they are dormant. Cost is often \$2 or less per tree when thousands are planted. Recently about six thousand cottonwood trees were planted in about four hours, using approximately 25 volunteers who planted about 30 cm deep in prepared soil using shovels.

## Augmenting Technologies

Several augmenting technologies can be used with phytoremediation, including irrigation to supply water, air sparging to move contaminants from the saturated zone to the vadose zone, bioventing to move contaminants below the root zone up into the rhizosphere, surfactant additions to solubilize contaminants to enhance biodegradation, other soil amendments (fertilizers) to enhance biodegradation, mechanical pumping to supplement evapotranspiration where plume control is needed, and fences or other barriers to control access to the site. Phytoremediation can be used as a polishing step in conjunction with other technologies, such as source removal, or integrated with other technologies as part of a site remediation. It is often an integral part of natural attenuation.

### **Critical Factors Affecting Performance**

Environmental conditions affect plant growth and biodegradation of the contaminants. Soil moisture should be on the order of 50 percent of field capacity for aerobic biodegradation to be effective. Oxygen transfer is poor if the soil is near saturation, whereas microbial growth and substrate transport are inhibited under particularly dry conditions.

The biodegradation and transport characteristics of the contaminants during phytoremediation are important. Volatile, nonbiodegradable contaminants may be released to the atmosphere, where they can be dispersed or transformed by light-catalyzed gas-phase reactions. Organic contaminants that have very low solubility in water may be difficult to treat because of their low bioavailability. Vegetation provides additional opportunities for sorption, so phytoremediation does not always proceed at a faster rate than bioremediation.

Temperature is an important variable, with rate reductions expected in winter, especially in cold climates. In addition, evapotranspiration rates also depend on water availability and humidity of the air at the site.

### **Monitoring**

There are several ways to monitor phytoremediation processes. Recently, Vroblesky *et al.* (1999) measured organic contaminants dissolved in fluids from core samples taken from trees. Their measurements demonstrated that the movement of contaminants into and through the vegetation proved that phytoremediation was occurring. Generally, it is difficult to detect contaminants in the atmosphere above the vegetation; however, contaminants in the gas phase have been measured in closed chambers and by using collection devices at the leaf surface or the soil surface. *In situ* monitoring methods using wells, lysimeters, or soil cores can also be used to monitor phytoremediation, just as they can be used to monitor other vadose remedial processes.

### **Status**

Phytoremediation has been used at many field sites where the goals are simple and the chances for success are great. Applications include biodegradation of petroleum hydrocarbons in the vadose zone, use of

vegetation to consume water and prevent migration of contaminants from the site, closure of landfills with vegetated caps, disposal of landfill leachate as irrigation water for trees, utilization of ammonium and nitrates in nitrogen rich soils, and riparian buffers to protect streams from contamination by agricultural fertilizers and pesticides.

## THE PERFORMANCE OF AVAILABLE REMEDIATION TECHNOLOGIES

The performance of *in situ* remedial methods depends on many factors, but geologic conditions, properties of the contaminants, and ability to access the subsurface are among the most critical. Many of these factors interact in complex ways to determine the viability of a particular remedial method at a particular site. Nevertheless, most remedial methods perform well under certain conditions but can be limited where geologic, contaminant, or access conditions differ from the ideal. The objective of this chapter is to identify the current state of remedial capabilities, the conditions that can be adequately addressed by current technology, and the conditions that represent gaps in remediation capabilities. To meet this objective, a list of the major critical factors affecting remedial performance has been compiled and evaluated to determine how each of these factors affects each of the available technologies. Table 7-16 summarizes the results of this evaluation.

Natural attenuation has recently been recognized as an important process for reducing risks associated with contaminants dissolved in ground water. This process is so important that natural attenuation is considered a viable option for remediating dissolved contaminants in some ground water plumes. The risk associated with some contaminants in the vadose zone probably also decreases with time due to natural processes, such as degradation by microbes, barometrically induced gas flow, or other processes. The state of knowledge about natural attenuation in the vadose zone is in its infancy compared to the understanding of processes in groundwater, however, and the extent to which this process may actually contribute to remediation is unclear. As a result, we have omitted natural attenuation as a remedial option in the following assessment. Additional research into this process may show that it is important and should be included as a viable alternative for remediation in the vadose zone.



**TABLE 7-16** Effects of various factors on remedial performance (*continued*).**Effects of contaminant properties on remedial performance.**

	SVE	Passive SVE	Thermal Conduction	Frequency	Radio	Steam	6-phase	Engineered Bio	Gas-phase Oxidant	Liquid Oxidant	Deep Soil Mixing	Reactive Barrier	Solidification Stabilization	Phyto-remediation
<b>Concentration in soil</b>														
High (>20000 mg/kg)	○	○	●	●	●	●	●	●	○	○	●	●	●	●
Moderate (10-20000)	●	●	●	●	●	●	●	●	●	●	●	●	●	●
Low (<10 mg/kg)	●	●	●	●	●	●	●	●	●	●	●	●	●	●
<b>Components</b>														
Dissolved phases only	●	○	●	●	●	●	●	○	●	●	●	●	●	●
Single NAPL	○	○	○	○	○	○	○	○	○	○	○	○	○	○
Multiple NAPL	○	○	○	○	○	○	○	○	○	○	○	○	○	○
NAPL and metals	○	○	○	○	○	○	○	○	○	○	○	○	○	○
<b>Time since release</b>														
Short (<1 yr)	●	●	●	●	●	●	●	●	●	●	●	●	●	●
Moderate (1-10yrs)	●	●	●	●	●	●	●	●	●	●	●	●	●	●
Long (>10 yrs)	○	○	○	○	○	○	○	○	○	○	○	○	○	○

**Effects of chemical properties on remedial performance.**

	SVE	Passive SVE	Thermal Conduction	Frequency	Radio	Steam	6-phase	Engineered Bio	Gas-phase Oxidant	Liquid Oxidant	Deep Soil Mixing	Reactive Barrier	Solidification Stabilization	Phyto-remediation
<b>A. Vapor:NAPL</b>														
High ( $V_p > 5$ mm Hg)	●	●	●	●	●	●	●	●	●	○	●	○	●	●
Intermed. (0.05-5 mm Hg)	○	○	●	●	●	●	●	●	○	●	●	●	●	●
Low ( $V_p < 0.05$ mm Hg)	○	○	●	○	○	○	○	●	○	●	●	●	●	●
<b>B. Air:water</b>														
High ( $H > 0.12$ )	●	●	●	●	●	●	●	●	●	○	●	●	●	●
Intermed. (0.01-0.12)	○	○	●	●	●	●	●	●	○	●	●	●	●	●
Low ( $H < 0.01$ )	○	○	●	●	●	●	●	●	○	●	●	●	●	●
<b>C. Solid:water</b>														
High ( $\log K_{oc} > 3.1$ )	○	○	●	○	○	○	○	○	○	○	●	●	○	○
Intermed. (2.0-3.1)	○	○	●	○	○	○	○	○	○	○	●	●	○	○
Low ( $\log K_{oc} < 2.0$ )	●	●	●	●	●	●	●	●	●	●	●	●	○	●
<b>D. NAPL:water</b>														
High ( $\log K_{ow} > 3.5$ )	●	●	●	●	●	●	●	○	●	●	●	●	●	○
Intermed. (2.5- 3.5)	●	●	●	●	●	●	●	○	●	●	●	●	●	○
Low ( $\log K_{ow} < 2.5$ )	●	●	●	●	●	●	●	●	●	●	●	●	●	●
<b>E. Molecular weight</b>														
High (>200 gm/mole)	○	○	●	○	○	○	○	○	○	○	●	○	●	○
Intermed. (110-200)	○	○	●	○	○	○	○	○	○	○	●	○	○	○
Low (<110 gm/mole)	○	○	●	○	○	○	○	○	○	○	●	○	○	○
<b>F. Halogenation</b>														
Hydrocarbon	●	●	●	●	●	●	●	●	●	●	●	●	●	○
1-3 halogens	●	●	●	●	●	●	●	○	●	●	●	●	○	○
>3 halogens	○	○	●	●	●	●	●	○	●	●	●	●	○	○

**TABLE 7-16** Effects of various factors on remedial performance (*continued*).

**Effects of access on remedial performance.**

	SVE	Passive SVE	Thermal Conduction	Radio Frequency	Stream	6-phase	Engineered Bio	Gas-phase Oxidant	Liquid Oxidant	Deep Soil Mixing	Reactive Barrier	Solidification Stabilization	Phyto-remediation	Natural Attenuation
<b>Depth</b>														
Surficial (<0.3 m)	○	○	●	●	○	●	●	○	●	○	○	●	●	●
Shallow (0.3-3m)	●	●	●	●	●	●	●	●	●	●	●	○	●	●
Moderate (3-10m)	○	○	○	○	○	○	○	○	○	○	○	○	○	○
Deep (>10 m)	●	●	●	●	●	●	●	●	●	○	●	○	○	●
<b>Areal Extent</b>														
Small (<1 acre)	●	●	●	●	●	●	●	●	●	●	●	●	●	●
Medium (1-10 acres)	●	●	○	○	○	○	○	○	○	○	○	○	○	○
Large (>10 acres)	○	○	○	○	○	○	○	○	○	○	○	○	○	○
Vertical drilling restricted	○	○	○	○	○	○	○	○	○	○	○	○	○	○
Surface access restricted	○	○	○	○	○	○	○	○	○	○	○	○	○	○
<b>Hazards to structures</b>														
Displacement	●	●	○	○	○	○	●	●	○	●	○	●	●	●
Heat	●	●	○	○	○	○	●	●	●	●	●	●	●	●
EM Fields	●	●	○	○	○	○	●	○	○	●	○	●	●	●
Chemical	○	●	●	●	○	●	○	○	○	●	○	●	●	●
<b>Duration until clean</b>														
Short (<1 yr)	○	○	●	●	●	●	○	●	●	●	○	○	○	○
Moderate (1-5 yrs)	●	○	●	●	●	●	○	●	●	●	○	○	○	○
Long (>5yrs)	●	●	●	●	●	●	●	●	●	●	●	●	●	○

**Legend**

●	Technology performance is unaffected by this factor. Technology can remediate vadose contamination to MCLs or similar regulatory goals under these conditions.
○	Some effect on performance. Technology can significantly reduce mass contained in, or mass flux out of, the vadose zone.
○	Major performance reduction expected. The technology can be expected to produce a limited reduction in mass contained in, or mass flux out of, the vadose zone.



## EVALUATION STRATEGY

The performance of each remedial method was evaluated by considering a hypothetical site where the technology could perform well. The effect of each factor was considered individually by estimating the extent to which it would diminish performance. Three levels of performance were considered in the evaluation of each factor. The highest level, which is indicated by a filled circle in Table 7-16, is where the factor has negligible detrimental effect on remedial performance when other conditions are favorable. The second level of performance, indicated by a circle and a central dot, recognizes some detrimental effect on performance that could lead to either significant delays or an inability to reach MCL-type goals. Nevertheless, significant reduction of mass or mobility of contaminants are possible using the technology under these conditions. The lowest level of performance, represented by an open circle, indicates a severe compromise of remedial capability. Typically, the technology is unable to provide a significant beneficial remedial effect under these conditions.

It is important to recognize that this evaluation strategy provides a simple way to match remedial technologies with the major factors affecting their performance, but it does so at the expense of overlooking a variety of important issues. Interactions between factors have been ignored, as have a variety of other circumstances that could influence performance at any particular site. In some cases, interactions of factors will conspire to reduce the performance more severely than indicated here. In other cases, several technologies could be combined synergistically to improve performance. Many current remedial actions combine several technologies in a sequence to maximize overall performance. The effects of interacting factors and the potential benefits of combining remedial technologies must be considered at any site, but such interactions and combinations are not considered here in order to limit the scope of the following summary. The evaluations were based on the results of field tests, where such results are known. However, field data are unavailable for many of the technologies under some of the conditions. In these cases, the performance of the technology was estimated based on lab experiments, theoretical estimates, or judgment.

The performance summary includes technologies that are described in the first part of this chapter. Documentation of the performance of

each technology is included in the previous sections and the reader should consult the papers cited in those sections for additional information about performance.

## **Hydrogeological Factors**

The hydrogeological factors considered in the evaluation include major rock type and average permeability of materials underlying the site, the effects of heterogeneity, flux of water through the vadose zone, average water saturation, presence of perched water, thickness of the capillary fringe, and the magnitude of fluctuations of the water table.

### **Media Type**

The type of rock or sediment that underlies a site affects remediation by influencing permeability, geochemistry, and access capabilities. These influences are considered explicitly themselves, but it is worthwhile to evaluate their effects as associated with rock type (Table 7-16). Clastic sediments underlie many sites. Grain size distribution is a major factor affecting remedial performance because it controls pore sizes and, hence, permeability. Fine-grained material implies low permeability and limited fluid flow, which may restrict the performance of remedial techniques based on gas or liquid flow. Thermal conduction and six-phase heating are exceptions as they can effectively heat clayey formations, and radio frequency (RF) heating will also heat any water-bearing horizon. Deep soil mixing is completely insensitive to grain size, and solidification/stabilization (S/S) of organics may actually benefit from the sorption of organic chemicals into fine-grained formations. Reactive barriers are well suited to fine-grained sediments because hydraulic fracturing performs well in this material, and because fine-grained formations typically have limited water flux. Plant growth may be limited in heavy clay, and natural attenuation may also be limited because of the relative isolation of contaminants in clays.

The performance of technologies that require fluid flow improves as the sediment coarsens. Most of the technologies that perform poorly in fine-grained sediments perform well in sand or gravel. Liquid oxidants may rapidly drain downward in gravel, limiting ability to maintain hydraulic control. The performance of hydraulic fractures in granular sediments has received limited investigation, so the effectiveness of

reactive barriers in sand and gravel is difficult to predict. Should hydraulic fracturing methods prove infeasible in coarse-grained unsaturated materials, jetting methods are an alternative.

Organic-rich sediments sorb contaminants, increasing the time required for remediation and affecting SVE and passive SVE, and also affecting heating technologies. The high temperatures developed during conduction heating should lessen the effect of sorption on organic-rich sediments. Bioremediation is affected because of organic-rich sediments' tendencies to reduce. Aerobic biochemical processes diminish as anaerobic ones are favored, so bioremediation could be either enhanced or diminished, depending upon the degradation reactions. Oxidants react with naturally occurring organic material, which diminishes the effectiveness of methods using oxidative fluids, as well as reactive barriers using oxidants. The ability for deep soil mixing to disrupt the subsurface is unaffected, but the potential limitations of SVE or oxidant injection used with deep soil mixing are similar to limitations for those processes separately. The performance of S/S can be diminished if organic-rich material interferes with the setting of cement. However, contaminants sorbed to organic material are less mobile than contaminants in clean soil, so the performance of S/S could improve. Phytoremediation probably is unaffected by the organic content of the soil. Natural attenuation may be affected by a decrease in contaminant mobility.

The performance of technologies involving fluid flow are affected by interbedded coarse- and fine-grained sediments, where recovery rates are limited by diffusion rates out of the fine-grained beds (contaminants are assumed to be distributed within both the fine- and coarse-grained beds). Electrical resistance heating is an exception, because it preferentially heats the fine-grained beds, accelerating the rate at which they release contaminants. RF heating also may perform well in interbedded sediments. The effects of thermal conduction are limited to the vicinity of the heating element, and so this technology is relatively insensitive to preferential flow in interbedded sediments. Deep soil mixing and S/S using excavation are insensitive to interbedded sediments. S/S done *in situ* may be severely affected by preferential flow, and probably will be ineffective in interbedded sediments.

The next three categories are hard rocks with different permeability structures. (Table 7-16). Volcanic rocks and lithified sedimentary rock

are expected to be relatively impermeable except along bedding planes and where they are cut by fractures. Unwelded tuffs are an exception, and they probably will behave more like clastic sediments during remediation. Crystalline rocks are expected to have even lower matrix permeabilities, and to be cut by fewer fractures than volcanic or clastic sedimentary rocks. Carbonate rocks have matrix permeabilities that range from moderate to low, but they commonly contain fractures enlarged by dissolution, and they may contain major karst conduits that will dominate flow.

All fractured rock materials are extremely difficult to remediate, and it is expected that remediation of karst will be infeasible using existing technologies. Deep soil mixing and S/S will be ineffective in hard rock due to difficulties with excavation. Conventional and passive SVE may be marginally effective in volcanic rock, but they probably will be ineffective in most hard rocks because of a high degree of heterogeneity. Heating should improve remedial performance, and there are a few cases where heating has apparently contributed to successful remediation in fractured rock. Bioremediation and the oxidant injection technologies will probably perform poorly because heterogeneities limit the ability to deliver fluids essential to performance. Gas and liquid phase oxidants probably will be ineffective in all three types of fractured rock because preferential flow will significantly increase the amount of oxidant required to react with the contaminants. It is feasible to create reactive barriers in rock using hydraulic fracturing methods, and it should be possible to create flat-lying barriers along flat-lying bedding planes. Therefore, it may be possible to create reactive barriers in some hard rocks, but there are no field data on this application. Phytoremediation and natural attenuation probably will be infeasible in fractured rock.

Gypsum-bearing strata are fairly common in the western United States, and sulfate-rich water is common in coal-mining areas throughout the United States. Gypsum-bearing rocks may contain solution cavities and channels that cause preferential flow much like karst does. However, gypsum may be present as a cement or as discontinuous bodies with limited solution channels. Remedial performance of the fluid flow technologies will be poor where solution channels are present. However, deep soil mixing, and, possibly, S/S should be feasible in gypsum, because it is friable and can be excavated or disrupted with an auger. Gypsum may interfere with the setting of cement, so the effects

on S/S are unclear. Sulfate-bearing water also affects organism growth and restricts the types of biochemical reactions that can be utilized during bioremediation. High sulfate concentrations may stunt or prevent plant growth during phytoremediation, and also may affect natural attenuation processes.

Peat is composed almost entirely of organic material that can strongly sorb organic contaminants (by contrast, it is assumed that organic-rich sediment is primarily clastic material with a subordinate fraction of organic substances). As a result, the effect of sorption reduces the performance of remedial technologies in peat even more than in organic-rich sediment.

### **Average Permeability and Heterogeneity**

The effects of the average permeability and the degree of heterogeneity on remediation follow from the principles outlined in the preceding pages. The effect of water content on relative permeability is ignored here; it will be considered later. Nearly all of the remedial technologies perform well in homogeneous, permeable material (Table 7-16). Reactive barriers are the one exception because of the uncertainty regarding methods for creating reactive barriers in permeable material. The flow rate of air through the subsurface decreases with average permeability, reducing the performance of SVE and passive SVE. Passive SVE may be ineffective in low permeability materials, although conventional SVE can perform well in some tight formations using high-suction pumps. Heating can extend the effectiveness of recovery techniques to lower permeabilities. Electrical resistance heating is well-suited to clay-rich formations, but it may be poorly suited to low-permeability formations lacking clay, such as unweathered crystalline rock. The performance of engineered bioremediation and the oxidant technologies is reduced with the permeability due to fluid delivery problems. Hydraulic fractures filled with permeable material improve the yields of wells in low permeability formations and should extend the performance of all of the technologies that rely on the delivery or recovery of fluids. Hydraulic fractures as an augmenting technology was not considered in this evaluation because they have only been used with a few of the remedial technologies. The performance of deep soil mixing and S/S should be independent of formation permeability, although S/S

that is done by injecting stabilizing fluids will only be feasible in high-to-moderate permeabilities.

Heterogeneity is perhaps the single most important factor affecting *in situ* remediation in the vadose zone. All the technologies perform well in homogeneous materials, and all the ones that rely on fluid flow perform poorly in heterogeneous formations (Table 7-16). Thermal conduction will reduce the effects of heterogeneities, but it cannot eliminate those effects altogether.

### Hydrologic Factors

Hydrologic factors control the amount and distribution of water at the site, affecting remediation in the vadose zone by influencing the relative permeability, accessibility, and natural flux of contaminants. The natural flux of water through the vadose zone, the typical air-filled porosity, presence of perched water, thickness of the capillary fringe, and extent of water table fluctuations are factors that can affect remediation (Table 7-16).

The dissolution of NAPL and migration of dissolved contaminants through the vadose zone increases with the average flux through the vadose zone. As a result, sites where the natural flux is relatively high are more vulnerable to groundwater contamination than sites with a low flux. This vulnerability may bias the consideration of clean-up time. Conventional and passive SVE, along with engineered bioremediation, phytoremediation, and natural attenuation may proceed at too slow a pace at sites that provide a significant and ongoing source of contaminants to the groundwater. The more aggressive technologies that can be applied quickly may be more appropriate. The thickness of reactive barriers must increase as the flux through the vadose zone increases, driving up the material costs.

Areas of particularly low flux will probably be relatively dry. A scarcity of water limits plant growth and may affect phytoremediation. Extremely dry conditions may slow SVE by increasing the sorption of contaminants, or it may slow bioremediation by limiting the availability of water. However, those effects are only important at extremely low moisture contents, which probably are rare even where the flux through the vadose zone is slow.

### Volumetric Gas Content

Volumetric gas content,  $\theta_a$ , (volume gas: total volume) is a critical factor affecting the movement and storage of gases in the subsurface, and it will control technologies that require gas flow, such as SVE, passive SVE, and gas-phase oxidant injection. Indeed, the performance categories of volumetric gas content in Table 7-16 were determined based on the performance of SVE; that is,  $\theta_a > 0.1$  will not limit SVE, but  $\theta_a < 0.05$  will severely limit SVE. The heating technologies are capable of changing the volumetric gas content, so they are relatively independent of this parameter. Most biostimulation processes in the vadose zone use gases to deliver nutrients, so the processes may be hampered by low values of  $\theta_a$ . It may be possible to deliver nutrients as liquids at vadose zone sites where  $\theta_a$  is small enough to preclude significant gas flow. The volumetric gas content is also called the air-filled porosity, and it can be estimated using the equation  $\theta_a = \phi (1 - S_w)$ , where  $S_w$  is the degree of water saturation and  $\phi$  is porosity.

### Perched Water

Perched water represents local saturated areas within the vadose zone where volumetric gas content and the gas-phase relative permeability are negligible. Contaminants in these areas are inaccessible to gas-flow methods. The performance of remedial methods based on gas flow are related to the amount of perched water at the site, and the methods probably will be ineffective where perched water is common. Heating may remove some perched water and improve performance compared to conventional SVE. Sites underlain by a vadose zone with many isolated zones of perched water may be difficult to remediate even using heating technologies unless characterization efforts are able to locate the perched zones (Table 7-16).

### Capillary Fringe and Water Table

The capillary fringe is inaccessible to technologies that rely on gas flow, so both a thick capillary fringe and a water table that fluctuates greatly diminishes the performance of those technologies. Thick capillary fringes occur in fine-grained formations, so a thick fringe also implies relatively low intrinsic permeability. Heating improves performance at the capillary fringe for the same reasons that it improves per-

formance in perched water zones. The low intrinsic permeability tacitly implied by a thick capillary fringe is expected to reduce the performance of the heating technologies (Table 7-16).

Large fluctuations of the water table may indicate that there is a significant section where the degree of saturation varies seasonally. This will cause problems with the technologies that rely on gas flow. It also may cause problems with the delivery of nutrients during engineered bioremediation. Those potentially detrimental effects can probably be addressed by artificially limiting the change in the water table using wells or dewatering trenches. However, dewatering increases both the initial and operational costs of remediation. Large fluctuations of the water table may affect phytoremediation because it places an additional restriction on the plants that are used—they must be able to both accomplish remediation and tolerate large changes of saturation in the root zone.

### **Contaminant Factors**

Clearly, properties of contaminants are among the most important factors affecting remedial performance. The location of contaminants is discussed in the previous section, where several geologic scenarios affecting location are evaluated. Location is also considered in the following section, where access issues related to the depth and size of the contaminated region are discussed. This section focuses on the contaminants themselves, the concentrations in which they occur, their basic components, age, and, most importantly, their basic chemical properties (Table 7-16).

The performance of remedial methods may depend on chemical factors that are interdependent; for example, the upper limit of concentration that can be remediated by a technology depends on key properties of the contaminant, such as vapor pressure. However, the evaluation method used here allows only one factor to be considered at a time. As a result, during the evaluation of each factor, assume that all the other factors, such as chemical properties, are typical of common contaminants that could be remediated by the technology; that is, the other factors will be non-limiting. It is beyond the scope of this summary to address all possible interactions, but some interactions between factors are presented where they are important.



### Concentration In Soil

Concentrations of common organic contaminants greater than 500 to 1000 mg/kg suggests the presence of NAPL phases in the soil, whereas lesser concentrations indicate that most of the organic contaminants occur as dissolved or adsorbed phases. The indicator of NAPL presence will shift to higher or lower concentrations with the solubility and  $K_d$  of the contaminant, but it is an important marker for estimating remedial performance. All of the remedial techniques are expected to perform well when low concentrations of dissolved contaminants are present. The performance of several remedial methods will decrease with increasing contaminant concentrations, particularly where NAPL is common (Table 7-16).

SVE can effectively remediate relatively high concentrations, perhaps as great as 20,000 mg/kg, of contaminants that are relatively volatile. High concentrations imply the existence of NAPL, so volatility of a single-component NAPL will be determined by its vapor pressure (partitioning between NAPL and vapor). Three categories of vapor pressure are presented below, and the 20,000 mg/kg upper bound is for compounds in the highest category of vapor pressure.

Passive SVE is intended for use in areas of relatively low concentrations, either along the periphery of a major plume or during the late stages of a remedial project. However, it is certainly feasible that significant mass can be removed or degraded using passive SVE in areas with moderate contaminant concentrations. Indeed, passive SVE may be ideal for areas that are remote or where access to electricity needed to power SVE blowers is unavailable. Higher contaminant concentrations generally mean longer remediation times for SVE because the volume of air that must flow through the site increases with the mass of contaminants that must be removed. However, extremely high concentrations may indicate locations of NAPL saturation where the air-filled porosity is occluded by NAPL. Such regions may inhibit air flow and, hence, removal will be slower. Gas-phase oxidants may also be unable to access areas saturated by NAPL. High vapor concentrations of solvents may also damage PVC well screens, piping, or other plastic exposed to the vapors.

A similar problem exists for the delivery of gas-phase nutrients for bioremediation, but this is by no means the only problem that high con-

centrations pose for bioremediation. Microbes can only utilize chemicals dissolved in water, so NAPL must first dissolve before it can be degraded biologically. In addition, compounds that can be readily degraded as dissolved phases of modest concentration may be toxic to microbes at high concentrations. Plants also are unable to access NAPL directly, and may find high concentrations toxic, depending on the type of plant and contaminant. There is evidence that some plants can tolerate relatively high concentrations of some NAPLs. High concentrations of NAPLs will not preclude phytoremediation altogether. However, in general, the ability of both bioremediation and phytoremediation to significantly reduce concentrations of NAPL is probably limited.

Heat increases the volatility of organic compounds, so the heating technologies perform better than conventional SVE in soils with high concentrations (Table 7-16). Like SVE, however, the upper bound of concentration increases with the vapor pressure of the contaminant, so technologies that can achieve the highest temperatures will perform better on areas with high concentrations of contaminants with low vapor pressure. Heating may also destroy organic contaminants by pyrolysis or oxidization, and these effects will improve remedial performance in soils of any concentration. Heating by conduction achieves the highest temperatures of the heating technologies, so it probably will be the most effective remediation method for areas of high concentrations, particularly where the contaminants have a low vapor pressure. However, heating by conduction affects only a relatively small region in the vicinity of the heater, so the applicability of the technique is subject to access limitations.

Liquid phase oxidants may be capable of degrading NAPL, but the details of this application are still being evaluated. It is possible that injection of liquid oxidants can destroy some NAPL, but degradation of high NAPL saturations is probably impractical.

The capability of reactive barriers filled with solid oxidants to degrade NAPL probably is similar to that of liquid oxidants. However, reactive barriers are intended to be relatively long-lived and to degrade contaminants that are naturally mobile, whereas liquid oxidants are intended to degrade all organic contaminants that can be quickly accessed soon after injection. In vadose zones where NAPL is trapped as ganglia, the primary mobile phase is probably dissolved in downward moving water. As a

result, reactive barriers may perform well in material with high NAPL concentrations, if the NAPL phase itself is immobile.

High concentrations of organic chemicals may interfere with the setting of cement during S/S, potentially limiting the applicability of this technology. Sorbants such as activated carbon may sufficiently isolate even relatively high concentrations of organic chemicals from the cement. Deep soil mixing will be insensitive to concentrations; however, the location of high concentrations must certainly be considered when designing the treatment method and depth of penetration used during DSM.

### **Components**

Contaminants may occur as single components, but commonly they exist as mixtures of multiple compounds. Such mixtures may affect remedial performance by diminishing the ability to target specific compounds that represent the major risk at a site. Moreover, many remedial technologies will rapidly recover or destroy contaminants with particular properties, while more recalcitrant compounds remain in the subsurface. This can be a serious issue where the recalcitrant compounds present serious risks, because the rapid reduction of overall contaminant mass may present an overly optimistic assessment of risk reduction.

The vapor pressure is greater over a single component NAPL than it is where the liquid occurs as a mixture. According to Raoult's Law, the depression of the vapor pressure is roughly proportional to the mole fraction of the NAPL in the mixture. As a result, volatile contaminants that occur as a minor component of a NAPL mixture may behave as if they have a significantly lower vapor pressure than the contaminant as a pure liquid. This effect of multi-component NAPL decreases the performance of both conventional and passive SVE, and it affects the performance of the heating techniques during recovery. The performance of conventional SVE is significantly curtailed, for example, where contaminants targeted for recovery occur at mole fractions of less than 0.01 (Table 7-16).

Bioremediation and phytoremediation are unable to access NAPL directly, and their performance is significantly diminished by the occurrence of either single components or NAPL mixtures. Moreover, both of those processes will selectively degrade some dissolved compounds while leaving other, more recalcitrant (and, perhaps, hazardous) com-

pounds behind. The oxidant injection technologies should be relatively insensitive to the components of NAPL because the strong oxidants used by those methods destroy many organic compounds. The occurrence of immobile NAPL should have a minor effect on the performance of reactive barriers, assuming that the barriers contain enough oxidant to react with whatever organic material becomes mobile. Some NAPLs may interfere with the setting of some S/S materials, but sorbants such as activated carbon can be used to effectively stabilize many NAPLs. Deep soil mixing is capable of performing well where both single component and mixtures of NAPL occur (Table 7-16).

The occurrence of hazardous metals, including radionuclides, along with NAPL is particularly problematic. Most of the vadose technologies are unable to remediate the metals in such mixtures. A two stage process, in which the NAPL is remediated by one technology (for example, by SVE) and the metals by another (for example, by S/S) is currently the most tenable approach to remediating areas containing mixed NAPL and metals. It is possible that deep soil mixing could be used to simultaneously remove organic chemicals and mix the resulting material with a stabilizing agent. Oxidants injected as a liquid, gas, or solid may also reduce the solubility and thereby immobilize some metals by changing their redox state. Furthermore, oxidants such as potassium permanganate can produce a residue (amorphous manganese oxide) that sorbs metals after they are reduced by reaction with organic compounds (Table 7-16).

### **Time Since Release**

The longer a contaminant resides in the subsurface, the more difficult it can be to remediate. Compounds occupy major flow channels soon after they are released to the environment, but with time they diffuse away to occupy small pores within matrix blocks between flow channels. The slow pace of diffusion back out of the matrix blocks can be a major limitation to the recovery of contaminants from fractured materials or interbedded sediments. The time available for contaminants to diffuse into the matrix blocks plays a key role in how deeply they penetrate the blocks, and how quickly they will diffuse back out. As a result, the time since a contaminant release has occurred can be an important factor affecting remediation.

All of the remedial methods perform best on contaminants that have been released for less than one year (Table 7-16). Performance diminishes with increasing time since release for all of the technologies, except deep soil mixing and S/S. The time since release will be less sensitive to the heating technologies because they can improve recovery from matrix blocks.

### Chemical Properties

The way in which a contaminant partitions among water, NAPL, vapor, and solid phases in the vadose zone is a factor that cuts across most of the other issues considered in this chapter. Technologies that access vapor phases perform better on compounds that readily partition into a vapor phase under almost any geologic condition. The following four partitioning coefficients, describing how a compound is distributed between any pair of either NAPL, water, vapor, or solid, are generally recognized to affect performance:

- Vapor pressure (NAPL:vapor)
- $K_{ow}$  or  $C_w$  (NAPL:water)
- $K_{oc}$  (water:solid)
- Henry's Law constant (water:vapor)

Vapor rarely contacts solids because most grain surfaces are covered by at least a thin film of water, and NAPLs generally fail to partition directly to solids, so the partitioning of vapor:solids and NAPL:solids is inconsequential during remediation.

Molecular weight and the number of halogen atoms in an organic molecule are important to some remedial processes; they also are evaluated.

The properties cited above span wide ranges of values among the common contaminants, and detailed evaluation of the properties was impractical. As a result, each of the properties is divided into three groups corresponding to large, intermediate, and small values, based on typical ranges. Thirty commonly occurring contaminants are listed in Table 7-17; their properties illustrate the three groupings of each property. The lists of contaminants are presented only as examples; they are by no means inclusive of all the chemicals in that range.

### Vapor: NAPL Partitioning

Partitioning between vapor and NAPL is characterized by vapor pressure. Pressures of 5 mm Hg and 0.05 mm Hg define the boundaries of three classes of vapor pressure in Table 7-16, based on guidelines accepted for the performance of conventional SVE. This grouping gives a rather narrow intermediate range of values, with the upper boundary between the vapor pressures of 1,2 dichlorobenzene and ethylbenzene, and the lower one between nitrobenzene and PCB-1242 (Table 7-17a). The vapor pressure of water is approximately 10 mm Hg.

Conventional SVE performs well on compounds in the upper range of vapor pressure, where  $P_{vap}$  is the limiting factor (for example, where NAPL recovery by SVE is an important part of remediation). Significant

**TABLE 7-17a** Examples of major contaminants classified by vapor pressure  
(from DeGrega et al. 1994; and EPA CFR Part 264, Appendix IX).

Compound	Vp mm Hg	Henry's Constant dimensionless	Log(K <sub>oc</sub> (mg/L))	Log K <sub>ow</sub>	Mw gm/mole	Halogens
Vinyl chloride	2,660	1.13E+00	1.76	1.38	62	1
1,1 DCE	600	9.27E-01	1.81	1.84	96	2
2,4,5 Trichlorophenol	400	7.16E-06	1.95	3.72	197	3
Acetone	270	1.74E-03	0.34	-0.24	58	0
1,1 DCA	180	2.39E-01	1.15	1.79	98	2
Chloroform	160	1.38E-01	1.49	1.97	119	3
Chlorobenzene	117	1.60E-01	2.52	2.84	112	1
1,1,1 TCA	100	1.66E-01	2.18	2.5	133	3
Benzene	95	2.26E-01	1.92	2.12	78	0
Carbon Tet	90	1.19E+00	2.04	2.64	153	4
MEK	77.5	1.90E-03	0.65	0.26	72	0
TCE	60	4.76E-01	2.10	2.38	131	3
PCE	60	1.09E+00	2.56	2.6	165	4
Toluene	22	2.41E-01	2.48	2.73	92	0
Xylene	10	1.70E-01	2.38	3.26	106	0
Ethylbenzene	7	3.27E-01	3.04	3.15	106	0
1,2 Dichlorobenzene	1	1.20E-01	3.23	3.60	147	2
Phenol	0.2	5.29E-05	1.15	1.46	94	0
Nitrobenzene	0.15	9.68E-04	1.56	1.85	123	0
PCB-1242	0.001	2.28E-02	3.73	4.11	261	6
Phenanthrene	9.60E-04	1.60E-03	4.15	4.46	178	0
Heptachlor	3.00E-04	6.02E-02	4.08	4.4	373	7
Pentachlorophenol	1.10E-04	1.14E-04	4.72	5	266	5
Hexachlorobenzene	1.90E-05	6.91E-02	3.59	5.23	284	6
Anthracene	1.70E-05	3.50E-03	3.15	4.45	178	0
Chlordane	1.00E-05	1.95E-03	5.15	3.32	409	8
Aldrin	6.00E-06	2.02E-02	3.98	5.3	364	6
DDT 4-4	1.90E-07	1.58E-03	5.39	6.19	354	5
Dieldrin	1.78E-07	2.38E-03	3.23	3.5	380	6
Benzo(a)pyrene	5.60E-09	1.99E-05	6.74	6.06	252	0

masses of contaminants in the intermediate range of vapor pressure can be recovered by SVE, but the time required to completely recover the NAPL may be excessive. SVE is generally ineffective at recovering NAPL with a vapor pressure less than 0.05 mm Hg. These guidelines are also generally applicable to the recovery of NAPL mixtures, where the mixture vapor pressure of a particular component is defined by Raoult's Law.

Vapor pressure increases with temperature, so the heating technologies perform better than conventional SVE when recovering contaminants with low vapor pressure. The effect of heating depends on the maximum temperatures that can be achieved by a particular technology, so conductive heating performs better than steam stripping on contaminants in the lowest vapor pressure category, since conductive heating creates hotter temperatures than steam stripping.

Technologies such as bioremediation, phytoremediation, liquid-phase oxidants and solid reactive barriers primarily act on dissolved contaminants. As a result, accessing contaminants that partition strongly into the vapor phase may be relatively difficult for these technologies.

The oxidant-based technologies are relatively new and, field data are sparse, so the details of their performance can only be inferred from basic principles. Deep soil mixing can be tailored to include processes that address a range of contaminant properties. As a result, deep soil mixing is less sensitive to vapor pressure to the other chemical properties as well.

Vapor phases are difficult to immobilize using S/S, so the performance of this technology probably will be poor where significant NAPLs occur with vapor pressures in the highest range.

### **Air:Water Partitioning**

The constant from Henry's Law, the ratio of the concentration of the compound in air to its concentration in water, characterizes the partitioning of a compound between air and water. Dimensionless Henry's constants (expressed on a mass basis of 0.12 and 0.01) define the three classes of partitioning between water and vapor (Table 7-16). The upper boundary occurs between the properties of 1,2 dichlorobenzene and chloroform, and the lower one occurs between anthracene and aldrin (Table 7-17b). These values were selected based on the performance of conventional SVE. In general, the retardation of vapors transported

**TABLE 7-17b**

**Examples of major contaminants classified by Henry's law constant**  
(from DeGrega et al. 1994; and EPA CFR Part 264, Appendix IX).

Compound	Vp mm Hg	Henry's Constant dimensionless	Log(Koc (mg/L))	Koc ml/gm	Mw gm/mole	Halogens
Carbon Tet	90	1.192	2.04	110	153	4
Vinyl chloride	2,660	1.131	1.76	57	62	1
PCE	60	1.090	2.56	364	165	4
1,1 DCE	600	0.927	1.81	65	96	2
TCE	60	0.476	2.10	126	131	3
Ethylbenzene	7	0.327	3.04	1,100	106	0
Toluene	22	0.241	2.48	300	92	0
1,1 DCA	180	0.239	1.15	14	98	2
Benzene	95	0.226	1.92	83	78	0
Xylene	10	0.170	2.38	240	106	0
1,1,1 TCA	100	0.166	2.18	152	133	3
Chlorobenzene	117	0.160	2.52	330	112	1
Chloroform	160	0.138	1.49	31	119	3
1,2 Dichlorobenzene	1	0.120	3.23	1,700	147	2
Hexachlorobenzene	1.90E-05	0.069	3.59	3,900	284	6
Heptachlor	3.00E-04	0.060	4.08	12,000	373	7
PCB-1242	0.001	0.023	3.73	5,370	261	6
Aldrin	6.00E-06	0.020	3.98	9,600	364	6
Anthracene	1.70E-05	0.0035	3.15	1,400	178	0
Dieldrin	1.78E-07	0.0024	3.23	1,700	380	6
Chlordane	1.00E-05	0.0019	5.15	1.40E+05	409	8
MEK	77.5	0.0019	0.65	4.5	72	0
Acetone	270	0.0017	0.34	2.2	58	0
Phenanthrene	9.60E-04	0.0016	4.15	14,000	178	0
DDT 4-4	1.90E-07	0.0016	5.39	2.43E+05	354	5
Nitrobenzene	0.15	9.68E-04	1.56	36	123	0
Pentachlorophenol	1.10E-04	1.14E-04	4.72	53,000	266	5
Phenol	0.2	5.29E-05	1.15	14.2	94	0
Benzo(a)pyrene	5.60E-09	1.99E-05	6.74	5.50E+06	252	0
2,4,5 Trichlorophenol	400	7.16E-06	1.95	89	197	3

through the subsurface is inversely proportional to  $H$  in materials where sorption is negligible, so three categories of Henry's constant correspond to different degrees of retardation during SVE. The degree of retardation also depends on the degree of saturation, according to  $R = 1 + S_w / (S_g H)$ . For example, where air occupies 50 percent of available pore space ( $S_w = S_g = 0.5$ ), a value of  $H = 0.1$  corresponds to a retardation factor of 11, whereas  $H = 0.01$  corresponds to a retardation factor of 101.

Heating technologies can be particularly effective at recovering contaminants with relatively low Henry's constants. Increasing the temperature will increase Henry's constant, so warming the subsurface will increase the mass of contaminant in the vapor phase. This effect occurs for any amount of heating. All of the heating technologies are capable of



increasing temperatures to the boiling point of water, however, and this has an important additional effect. Boiling results in a roughly 1,000 fold increase in the volume of water. As a result, the mass of a contaminant that can be dissolved in one gram of water vapor is 1,000 times greater than the mass dissolved in one gram of liquid water. This effect causes dissolved contaminants with all but the very lowest Henry's constants to partition strongly into the vapor phase when pore water is heated to steam temperatures.

Air:water partitioning is rarely a factor during bioremediation. Biochemical reactions cannot directly access vapor phases, so contaminants with a high value of  $H$  may have significant masses beyond the reach of degradation reactions. This could be an issue where those vapors are naturally mobile, but in most cases vapors will partition back into the water phases as biodegradation takes place.

Gas-phase oxidant injection should perform best on contaminants with a high value of  $H$ . Liquid-phase oxidant injection and reactive barriers should perform best on contaminants with a low value of  $H$ , although these forecasts are speculative. S/S may perform poorly for contaminants with a high  $H$ , because it is unable to immobilize vapor phases.

Phytoremediation performs well for all values of  $H$ . Compounds with low values of  $H$  are dissolved where they are available for degradation by microbes in the rhizosphere, whereas compounds with high values of  $H$  are transpired through leaves and dissipated into the atmosphere.

### **Solid:Water Partitioning**

Contaminant partitioning between solid surfaces and water is determined by sorption characteristics of the soil and contaminant. Most sorption of organic chemicals is assumed to occur on natural organic material, so the partitioning between organic carbon and water is used to predict sorption onto soil. The organic carbon partitioning coefficient,  $K_{oc}$ , is the ratio of the concentration of a compound sorbed to organic carbon in equilibrium with a dissolved phase, and the partitioning coefficient of the soil itself is the product of  $K_{oc}$  and the organic fraction of the soil.

Sorption contributes to the retardation of vapor transport. For example, the retardation factor due to sorption alone is  $R = 1 + .13 K_{oc}/H$  for a sediment where density = 2.0 gm/cm<sup>3</sup>; porosity = 0.3; saturation = 0.5;

and organic carbon fraction=0.01. Previously it was assumed that the effects of  $H$  on retardation of this typical soil were small where  $H$  is greater than 0.12, and that SVE performance could be affected where  $R$  is greater than 10, suggesting that the retardation of contaminants could be significant where  $K_{oc}$  is greater than 10 mg/l. Almost all of the contaminants have a  $K_{oc}$  greater than 10 mg/l, and some of them are many orders of magnitude greater than that, so it is clear that sorption could be an important limitation to SVE performance. The intermediate category of  $K_{oc}$  is bounded  $2.0 < \log K_{oc} \text{ (mg/l)} < 3.1$  (Table 7-17c). In general,  $R$  depends on both  $K_{oc}$  and  $H$ , and these two partitioning coefficients are independent. As a result, the retardation factor of compounds in the high category of  $K_{oc}$  are all quite large, but  $R$  cannot be predicted from  $K_{oc}$  alone in the intermediate and low values of  $K_{oc}$ , due to the effect that  $H$  has on  $R$ .

TABLE 7-17c

**Examples of major contaminants classified by organic carbon partitioning coefficient** (from DeGrega eta l. 1994; and EPA CFR Part 264, Appendix IX).

Compound	Vp mm Hg	Henry's Constant dimensionless	Log(Koc[ml/g])	Log Kow	Mw gm/mole	Halogens
Acetone	270	1.74E-03	0.34	-0.24	58	0
MEK	77.5	1.90E-03	0.65	0.26	72	0
1,1 DCA	180	2.39E-01	1.15	1.79	98	2
Phenol	0.2	5.29E-05	1.15	1.46	94	0
Chloroform	160	1.38E-01	1.49	1.97	119	3
Nitrobenzene	0.15	9.68E-04	1.56	1.85	123	0
Vinyl chloride	2,660	1.13E+00	1.76	1.38	62	1
1,1 DCE	600	9.27E-01	1.81	1.84	96	2
Benzene	95	2.26E-01	1.92	2.12	78	0
2,4,5 Trichlorophenol	400	7.16E-06	1.95	3.72	197	3
Carbon Tet	90	1.19E+00	2.04	2.64	153	4
TCE	60	4.76E-01	2.10	2.38	131	3
1,1,1 TCA	100	1.66E-01	2.18	2.5	133	3
Xylene	10	1.70E-01	2.38	3.26	106	0
Toluene	22	2.41E-01	2.48	2.73	92	0
Chlorobenzene	117	1.60E-01	2.52	2.84	112	1
PCE	60	1.09E+00	2.56	2.6	165	4
Ethylbenzene	7	3.27E-01	3.04	3.15	106	0
Anthracene	1.70E-05	3.50E-03	3.15	4.45	178	0
1,2 Dichlorobenzene	1	1.20E-01	3.23	3.60	147	2
Dieldrin	1.78E-07	2.38E-03	3.23	3.5	380	6
Hexachlorobenzene	1.90E-05	6.91E-02	3.59	5.23	284	6
PCB-1242	0.001	2.28E-02	3.73	4.11	261	6
Aldrin	6.00E-06	2.02E-02	3.98	5.3	364	6
Heptachlor	3.00E-04	6.02E-02	4.08	4.4	373	7
Phenanthrene	9.60E-04	1.60E-03	4.15	4.46	178	0
Pentachlorophenol	1.10E-04	1.14E-04	4.72	5	266	5
Chlordane	1.00E-05	1.95E-03	5.15	3.32	409	8
DDT 4-4	1.90E-07	1.58E-03	5.39	6.19	354	5
Benzo(a)pyrene	5.60E-09	1.99E-05	6.74	6.06	252	0

The performance of SVE in most sediments is expected to be largely unaffected by sorption of compounds in the lowest category of  $K_{oc}$ . However, sorption of even those compounds in the lowest category of  $K_{oc}$  may significantly affect SVE performance in soils that are particularly rich in organic carbon. At the other end of the scale, sorption significantly retards recovery and may severely reduce the effectiveness of conventional SVE for contaminants in the highest category of  $K_{oc}$ . Sorption of contaminants in the intermediate group can delay remediation goals. This is a particularly important factor during the late stages of a project when the change of concentration is relatively slow.

Heating enhances desorption of contaminants, so the performance of heating technologies with SVE is better than conventional SVE (without heating). This effect is most important for contaminants with low-to-intermediate  $K_{oc}$  values. High temperatures may be required to desorb compounds with a high  $K_{oc}$ , so conductive heating may perform better than the other heating technologies when recovering strongly sorbed contaminants.

The performance of bioremediation and phytoremediation diminishes as  $K_{oc}$  increases because bioavailability can be significantly diminished where contaminants are strongly sorbed to organic matter. The performance of oxidant injection technologies is expected to diminish with the degree of sorption. Remediation of strongly sorbed contaminants could be accomplished by oxidizing all the organic material available for sorption, but this would increase the amount of oxidant required.

The performance of deep soil mixing and *in situ* reactive barriers are insensitive to sorption characteristics. Deep soil mixing has enough flexibility to address strongly sorbed contaminants. Reactive barriers are designed to degrade mobile compounds, so strongly sorbed contaminants take longer to contact the reactive material.

Sorption is actually an advantage to S/S systems, where sorbents such as activated carbon are used to bind organic chemicals as part of the remediation process. This is the only remedial technology in which performance improves as  $K_{oc}$  of the target contaminant increases.

Organic chemicals may sorb directly to the surfaces of minerals such as clays. This effect may be particularly important in clayey formations with a minute fraction of organic carbon. The degree of sorption to minerals cannot be gauged by  $K_{oc}$  values, so it is possible that sorption to clays will delay remediation even more than suggested here. The rela-

tive performance of the remedial methods should be independent of the site of sorption.

### **Solubility and NAPL:Water Partitioning**

Partitioning of a compound between an NAPL and aqueous phase can be described by several parameters, but the octanol:water partitioning coefficient,  $K_{ow}$ , is used here. This value gives the ratio of equilibrium concentrations of a compound dissolved in octanol to that dissolved in water. The solubility of an organic chemical is related to  $K_{ow}$ , and an evaluation based on solubility is similar to one based on  $K_{ow}$ . High values of  $K_{ow}$  indicate the chemical is hydrophobic and correspond to low aqueous solubilities, whereas low values of  $K_{ow}$  correspond to high aqueous solubilities.

Octanol:water partitioning coefficients span more than six orders of magnitude, from less than 1 to more than  $10^6$ . An intermediate group of  $\log(K_{ow})$  ranging from  $2.5 < \log K_{ow} < 3.5$  splits the typical contaminants into three groups of roughly equal numbers of contaminants (Table 7-17d).

Engineered bioremediation and phytoremediation, the remedial methods most strongly affected by  $K_{ow}$ , perform well on contaminants with a low  $K_{ow}$  because these contaminants will be readily available in an aqueous phase. Contaminants with a high  $K_{ow}$  may not be bioavailable.

The performance of the other remedial methods are largely independent of the  $K_{ow}$  of target contaminants

### **Molecular Weight**

Molecular weights of common contaminants range from 50 to more than 400 gm/mole. Contaminants with a molecular weight less than 110 gm/mole are considered light, whereas those with a molecular weight greater than 200 are considered heavy (Table 7-16). The upper boundary occurs between xylene and chlorobenzene, and the lower one occurs between 2,4,5-trichlorophenol and benzopyrene (Table 7-17e).

Molecular weight affects remedial performance because it is indirectly related to several other properties. In general, as molecular weight increases, the vapor pressure decreases, as does the Henry's constant. Both the  $K_{oc}$  and the  $K_{ow}$  typically increase with molecular weight. There are certainly exceptions to these generalizations. For example,

**TABLE 7-17d**

**Examples of major contaminants classified by Octanol:water partitioning coefficient** (from DeGrega et al. 1994; and EPA CFR Part 264, Appendix IX).

Compound	Vp mm Hg	Henry's Constant dimensionless	Log(K <sub>oc</sub> (mg/L))	Log K <sub>ow</sub>	Mw gm/mole	Halogens
DDT 4-4	1.90E-07	1.58E-03	5.39	6.19	354	5
Benzo(a)pyrene	5.60E-09	1.99E-05	6.74	6.06	252	0
Aldrin	6.00E-06	2.02E-02	3.98	5.30	364	6
Hexachlorobenzene	1.90E-05	6.91E-02	3.59	5.23	284	6
Pentachlorophenol	1.10E-04	1.14E-04	4.72	5.00	266	5
Phenanthrene	9.60E-04	1.60E-03	4.15	4.46	178	0
Anthracene	1.70E-05	3.50E-03	3.15	4.45	178	0
Heptachlor	3.00E-04	6.02E-02	4.08	4.40	373	7
PCB-1242	1.00E-03	2.28E-02	3.73	4.11	261	6
2,4,5 Trichlorophenol	400	7.16E-06	1.95	3.72	197	3
1,2 Dichlorobenzene	1	1.20E-01	3.23	3.60	147	2
Dieldrin	1.78E-07	2.38E-03	3.23	3.50	380	6
Chlordane	1.00E-05	1.95E-03	5.15	3.32	409	8
Xylene	10	1.70E-01	2.38	3.26	106	0
Ethylbenzene	7	3.27E-01	3.04	3.15	106	0
Chlorobenzene	117	1.60E-01	2.52	2.84	112	1
Toluene	22	2.41E-01	2.48	2.73	92	0
Carbon Tet	90	1.19E+00	2.04	2.64	153	4
PCE	60	1.09E+00	2.56	2.60	165	4
1,1,1 TCA	100	1.66E-01	2.18	2.50	133	3
TCE	60	4.76E-01	2.10	2.38	131	3
Benzene	95	2.26E-01	1.92	2.12	78	0
Chloroform	160	1.38E-01	1.49	1.97	119	3
Nitrobenzene	0.15	9.68E-04	1.56	1.85	123	0
1,1 DCE	600	9.27E-01	1.81	1.84	96	2
1,1 DCA	180	2.39E-01	1.15	1.79	98	2
Phenol	0.20	5.29E-05	1.15	1.46	94	0
Vinyl chloride	2,660	1.13E+00	1.76	1.38	62	1
MEK	78	1.90E-03	0.65	0.26	72	0
Acetone	270	1.74E-03	0.34	-0.24	58	0

phenol is relatively light but has an exceptionally low Henry's constant, and chlorobenzene is of intermediate weight but has a relatively high vapor pressure. Nevertheless, in most cases, increasing molecular weight increases partitioning into either NAPL phases or onto the surfaces of solids, markedly affecting remediation performance.

All of the technologies except S/S perform best on compounds with low molecular weight. The partitioning effects that accompany an increase in molecular weight slow conventional SVE, and relatively heavy compounds cannot be remediated by SVE. Heating helps partition molecules into the vapor phase, so the performance of SVE on heavier organic molecules can be improved using heating technologies. Some heavy compounds can be oxidized in place by high temperatures created by conductive heating. The bioavailability of heavy molecules is

**TABLE 7-17e** Examples of major contaminants classified by molecular weight (from DeGrega et al. 1994; and EPA CFR Part 264, Appendix IX).

Compound	Vp mm Hg	Henry's Constant dimensionless	Log(Koc (mg/L))	Log Kow	Mw gm/mole	Halogens
Acetone	2.70E+02	1.74E-03	0.34	-0.24	58	0
Vinyl chloride	2.66E+03	1.13E+00	1.76	1.38	62	1
MEK	7.75E+01	1.90E-03	0.65	0.26	72	0
Benzene	9.50E+01	2.26E-01	1.92	2.12	78	0
Toluene	2.20E+01	2.41E-01	2.48	2.73	92	0
Phenol	2.00E-01	5.29E-05	1.15	1.46	94	0
1,1 DCE	6.00E+02	9.27E-01	1.81	1.84	96	2
1,1 DCA	1.80E+02	2.39E-01	1.15	1.79	98	2
Ethylbenzene	7.00E+00	3.27E-01	3.04	3.15	106	0
Xylene	1.00E+01	1.70E-01	2.38	3.26	106	0
Chlorobenzene	1.17E+02	1.60E-01	2.52	2.84	112	1
Chloroform	1.60E+02	1.38E-01	1.49	1.97	119	3
Nitrobenzene	1.50E-01	9.68E-04	1.56	1.85	123	0
TCE	6.00E+01	4.76E-01	2.10	2.38	131	3
1,1,1 TCA	1.00E+02	1.66E-01	2.18	2.50	133	3
1,2 Dichlorobenzene	1.00E+00	1.20E-01	3.23	3.60	147	2
Carbon Tet	9.00E+01	1.19E+00	2.04	2.64	153	4
PCE	6.00E+01	1.09E+00	2.56	2.60	165	4
Anthracene	1.70E-05	3.50E-03	3.15	4.45	178	0
Phenanthrene	9.60E-04	1.60E-03	4.15	4.46	178	0
2,4,5 Trichlorophenol	4.00E+02	7.16E-06	1.95	3.72	197	3
Benzo(a)pyrene	5.60E-09	1.99E-05	6.74	6.06	252	0
PCB-1242	1.00E-03	2.28E-02	3.73	4.11	261	6
Pentachlorophenol	1.10E-04	1.14E-04	4.72	5.00	266	5
Hexachlorobenzene	1.90E-05	6.91E-02	3.59	5.23	284	6
DDT 4-4	1.90E-07	1.58E-03	5.39	6.19	354	5
Aldrin	6.00E-06	2.02E-02	3.98	5.30	364	6
Heptachlor	3.00E-04	6.02E-02	4.08	4.40	373	7
Dieldrin	1.78E-07	2.38E-03	3.23	3.50	380	6
Chlordane	1.00E-05	1.95E-03	5.15	3.32	409	8

generally poor, so the effectiveness of bioremediation and phytoremediation on heavy molecules is limited. Some methods of treating heavy organic molecules with oxidants or other compounds to break them into smaller molecular fragments show promise in improving bioavailability. The oxidant technologies may destroy large organic molecules, but there are issues related to the daughter products of these reactions that must be resolved.

### Halogenation

The degree of halogenation ranges from hydrocarbons, which lack any halogens, through moderately halogenated molecules with as many as 3 halogens, to highly halogenated molecules with 4 or more halogen atoms in their molecular formula (Table 7-17f).

**TABLE 7-17f**

**Examples of major contaminants classified by halogen atoms** (from DeGrega et al. 1994; and EPA CFR Part 264, Appendix IX).

Compound	Vp mm Hg	Henry's Constant dimensionless	Log(Koc (mg/L))	Log Kow	Mw gm/mole	Halogens
Acetone	2.70E+02	1.74E-03	0.34	-0.24	58	0
Vinyl chloride	2.66E+03	1.13E+00	1.76	1.38	62	1
MEK	7.75E+01	1.90E-03	0.65	0.26	72	0
Benzene	9.50E+01	2.26E-01	1.92	2.12	78	0
Toluene	2.20E+01	2.41E-01	2.48	2.73	92	0
Phenol	2.00E-01	5.29E-05	1.15	1.46	94	0
1,1 DCE	6.00E+02	9.27E-01	1.81	1.84	96	2
1,1 DCA	1.80E+02	2.39E-01	1.15	1.79	98	2
Ethylbenzene	7.00E+00	3.27E-01	3.04	3.15	106	0
Xylene	1.00E+01	1.70E-01	2.38	3.26	106	0
Chlorobenzene	1.17E+02	1.60E-01	2.52	2.84	112	1
Chloroform	1.60E+02	1.38E-01	1.49	1.97	119	3
Nitrobenzene	1.50E-01	9.68E-04	1.56	1.85	123	0
TCE	6.00E+01	4.76E-01	2.10	2.38	131	3
1,1,1 TCA	1.00E+02	1.66E-01	2.18	2.50	133	3
1,2 Dichlorobenzene	1.00E+00	1.20E-01	3.23	3.60	147	2
Carbon Tet	9.00E+01	1.19E+00	2.04	2.64	153	4
PCE	6.00E+01	1.09E+00	2.56	2.60	165	4
Anthracene	1.70E-05	3.50E-03	3.15	4.45	178	0
Phenanthrene	9.60E-04	1.60E-03	4.15	4.46	178	0
2,4,5 Trichlorophenol	4.00E+02	7.16E-06	1.95	3.72	197	3
Benzo(a)pyrene	5.60E-09	1.99E-05	6.74	6.06	252	0
PCB-1242	1.00E-03	2.28E-02	3.73	4.11	261	6
Pentachlorophenol	1.10E-04	1.14E-04	4.72	5.00	266	5
Hexachlorbenzene	1.90E-05	6.91E-02	3.59	5.23	284	6
DDT 4-4	1.90E-07	1.58E-03	5.39	6.19	354	5
Aldrin	6.00E-06	2.02E-02	3.98	5.30	364	6
Heptachlor	3.00E-04	6.02E-02	4.08	4.40	373	7
Dieldrin	1.78E-07	2.38E-03	3.23	3.50	380	6
Chlordane	1.00E-05	1.95E-03	5.15	3.32	409	8

The degree of halogenation affects the susceptibility to bioremediation. Hydrocarbons are readily degraded by microbes, and compounds with a few halogen atoms in their structure may be degraded under some conditions. Compounds with many halogens are typically recalcitrant and are the most difficult to remediate biologically.

Increasing halogenation has effects on partitioning similar to molecular weight increase, affecting remediation in the same way as molecular weight. The degree of halogenation is expected to play a role in degradation reactions and to affect the performance of remediation by *in situ* oxidization. Details of the oxidization reactions are difficult to generalize based solely on the degree of halogenation.

## Access

All of the remedial processes currently available require some type of access to the contaminated region. Typically, well boring provides access to contaminants, so many access issues are closely related to the cost and performance of wells. Several notable exceptions are outlined below and are considered in Table 7-16.

## Depth

Contaminants in the vadose zone typically occur at depths less than 100 m, and most of them at less than 10 m. The shallowest contaminants, those in surficial sediments at depths less than 0.3 m, cannot be treated by many of the processes discussed here (surficial sediments can be excavated and treated using *ex situ* methods, which are not discussed in this chapter). Phytoremediation is an important exception, performing best at these shallow depths. Bioremediation using land-farming methods is ideally suited to surficial contamination, particularly when aerobic biochemical reactions can be used to degrade the contaminants. Surficial soils are effectively heated by conduction using thermal blankets, but this is the only heating technology that is intended for such shallow depths. S/S is well-suited to surficial soils because they can be readily accessed by excavation. A variety of other processes that treat excavated soil, such as thermal desorption and incineration, can be used to remediate surficial materials.

Shallow contaminants, at depths of 0.3 to 3 m, can be accessed by SVE vents. There can be problems sealing vents against leakage between the casing and the surrounding media at shallow depth. Moreover, the zone of influence of an SVE vent typically increases with depth, and shallow wells affect a relatively small area. A low permeability layer between the well screen and the ground surface extends the radius of influence, but constructing such a layer increases cost. Heating technologies are effective at shallow depths. Land-farming methods are inapplicable at depths below 0.3 m, but other methods can be used to deliver nutrients for engineered bioremediation. In general, bioremediation can be used with enough different delivery methods so that its application is independent of depth (Table 7-16).

Gas-phase oxidants can be used at shallow depths, but the radius of influence of wells used for oxidant injection may limit performance just



as it does for SVE. Macropores common near the ground surface may also affect the flow of gases and limit the performance of SVE and oxidant injection. Liquid oxidants are typically injected through a lance, which can be used at shallow depths. It is possible to apply liquid oxidants to surficial soils as well. Reactive barriers can be readily created in many shallow soils, but they generally are not applicable at depths less than about 1.5 m due to limitations of hydraulic fracturing. In principle, passive SVE can be used at shallow depths, but the short distance between the well screen and ground surface may be too small to sustain barometric pumping. Phytoremediation may be applicable at shallow depths (0.3 to 3 m), but the effectiveness at the bottom of this depth range requires the use of plants with relatively deep root systems.

Most of the technologies perform well at moderate depths (3-10 m). S/S is possible at these depths, but costs to mix the stabilizing material with the contaminants increases over this range. Phytoremediation is probably infeasible at moderate depths, except possibly under special circumstances where extremely deep-rooted plants are available (Table 7-16).

The same performance trends occur at depths below 10 m; all of the technologies except S/S and phytoremediation should perform well. It is technically feasible to conduct deep soil mixing below 10 m, but the cost of using equipment that can mix at these depths typically confines this technique to shallower regions.

Drilling costs can become a major factor as depth increases, so there will be a cost advantage to technologies that can minimize the number of wells required to treat an area. This will be particularly important at extremely deep sites, or where drilling is expensive for reasons other than well depth. The distance that can be affected by an individual SVE vent increases with depth and SVE requires fairly simple well completions that can be readily installed at any depth. It is not surprising, therefore, that SVE has been conducted at some of the deepest vadose zone sites. Steam injection is capable of affecting a larger volume of ground per well than the other heating technologies, so it will have advantages where wells are expensive.

### **Areal Extent**

The areal extent of contaminants does not affect remedial performance, but it does impact cost. This is particularly relevant to the more

aggressive technologies that are designed to treat high concentrations in source zones within the vadose zone, where performance is obtained by relatively expensive methods. A detailed cost evaluation of the various technologies is beyond the scope of this chapter, but relative costs are reflected in the applicability to large contaminated areas.

All of the remedial methods are applicable at relatively small sites with areas less than 1 acre (Table 7-16). Conventional SVE and many of the heating technologies are applicable at intermediate-sized sites with areas between 1 and 10 acres. In general, the larger sites are best addressed by *in situ* techniques if they are underlain by a thick, permeable vadose zone with a low permeability layer near the ground surface, because such conditions increase the radius of influence of extraction vents. Conductive heating requires closely spaced wells, however, so it probably is limited to smaller sites. Applications of RF and six-phase heating have been limited to relatively small sites, so possible economies of scale are unclear. The oxidant injection technologies and reactive barriers are primarily intended to address small source zones, but could be used at intermediate-sized sites. Deep soil mixing is usually too expensive for intermediate-sized sites. S/S methods are widely used for intermediate-sized sites, but only where the soil can be excavated, mixed with the stabilizing material, and returned to the site.

It is feasible to use conventional SVE at some large sites because this technology is well known, and technology-specific surface equipment is widely available and robust. Passive SVE, however, is particularly well-suited to large sites because of its practically negligible operating costs. Steam stripping may be applicable to large sites under special circumstances, such as high NAPL saturations and low-volatility contamination. Bioremediation is applicable to large sites, particularly where land-farming methods can be used. Phytoremediation, where feasible based on other constraints, is also well-suited to large sites (Table 7-16).

### **Vertical Drilling Restrictions**

Vertical drilling is restricted at many locations due to the presence of buildings, overhead electrical cables, or buried utilities. The adaptation of directional drilling technology from the utility installation industry during the past decade has provided a viable alternative to vertical wells. Horizontal wells are more expensive than vertical wells, but a single horizontal well can access a contaminated volume several times greater

than a vertical well, so the cost differences may be offset by the improved performance. Nevertheless, most applications of horizontal wells have been justified by their ability to access beneath structures, rather than by an improvement in performance.

Horizontal or directional wells can be used with many vadose remedial technologies where the contaminated region cannot be accessed by vertical wells. The use of horizontal wells may increase costs for initial installation and design of those technologies. However, it is a key enabling technology where structures restrict access to a vertical drill rig.

Several technologies are infeasible where vertical drilling is impossible (Table 7-16). Deep soil mixing relies on a large vertical auger that is impossible to use where vertical drilling is restricted. The closely spaced heating wells used during conduction heating are infeasible to install without vertical drilling, but it would be possible to use thermal blankets in some areas where vertical drilling was restricted. The standard configuration of six electrodes around a central well used for 6-phase heating would be impractical to use without vertical drilling. Liquid oxidants are typically injected from a lance driven vertically into the subsurface. It is possible to deliver liquid oxidants from a horizontal well, but the well spacing required to adequately disperse liquid oxidant in the vadose zone would be so small that the use of horizontal wells would be impractical in most situations. S/S would probably be impractical anywhere that vertical drilling is restricted. Drilling restrictions would have no effect on phytoremediation.

### **Surface Access Restricted**

The ground surface cannot be accessed at all at some sites, placing even more restrictions on remediation (Table 7-16). Technologies that can use horizontal wells are still applicable, although the lack of any surface access will require the use of a more sophisticated location system during drilling. Conductive heating, S/S and phytoremediation will be infeasible without access to the ground surface.

### **Hazards To Structures**

Remediation processes present a variety of hazards to structures in the vicinity. Displacements, heating, electromagnetic fields, and chemi-

cals are possible hazards to structures (buildings, utilities, storage tanks) or people working or living in nearby buildings (Table 7-16).

Displacements can be created by injecting fluid or by severe desiccation. Hydraulic fracturing methods used to create reactive barriers are known to create vertical displacements over the fractures. Other techniques involving fluid injection also cause displacement, but this is minor as long as injection pressures are low enough to prevent fracturing. Drying sediments during heating may cause subsidence in the overlying ground, particularly where the sediments are clay-rich. Thermal expansion could also result in unwanted displacements during heating.

The heating technologies clearly are impractical near structures that are sensitive to temperature changes, like fuel storage tanks.

RF heating is the only technology that is impossible to use near structures that are sensitive to electromagnetic fields. However, EM fields associated with the other electrical heating technologies may also eliminate them from use near sensitive structures.

Most of the remedial technologies present some risk of chemical exposure, but this factor probably significantly affects only those technologies involving fluid injection. In those cases, contaminants mobilized during injection could present a hazard to neighboring structures. Gas- and liquid-phase oxidant injection presents the most serious risk, since the oxidant itself is both highly mobile and potentially hazardous. Methods for containing injected fluids are well-known, and this issue should receive a great deal of attention during the design and implementation of remedial processes. As a result, the risks of chemical exposure during implementation of these remedial methods can generally be reduced by implementing the appropriate engineering measures.

Deep soil mixing and S/S can mobilize contaminant vapors that may present a risk to nearby structures. However, the installation methods required to implement those techniques are difficult to deploy near structures.

### **Acceptable Duration Until Clean**

Remedial efforts are commonly driven by strict time schedules. Several of the technologies can be implemented in a few days to months, while others require several years or longer. Clearly, the time required to complete remediation depends on both type and amount of contaminant present, and a variety of other geologic factors.

All of the technologies can be effective if they are given a relatively long time to remediate conditions. Passive SVE and phytoremediation are the least energy intensive of the technologies considered, and they will probably take longest to clean a site (Table 7-16).

The time required for reactive barriers to clean a site will depend on the ambient rate of mass transfer within the site. It is possible that reactive barriers significantly reduce the flux of contaminants from the vadose zone quickly, even though immobile contaminants may remain above the barriers for much longer times. Data documenting the long-term performance of reactive barriers in the vadose zone are not yet available for this new technology.

Conventional SVE projects are commonly completed within 1 to 5 years, and many engineered bioremediation efforts are completed within this span as well. It is possible for those technologies to be effective more quickly at small sites containing low concentrations of contaminants.

All of the heating technologies, the oxidant injection methods, deep soil mixing, and S/S are completed within a short period of time, typically less than 1 year.

## **GAPS IN CURRENT CAPABILITIES**

Currently available technologies can remediate many commonly occurring conditions, but gaps in these capabilities plague the efforts to reduce risks at contaminated sites. The performance review of remedial technologies presented in this section identified key factors related to geology, contaminant properties, and access that underlie these gaps in capabilities.

Heterogeneity is the single most important geological factor that limits the performance of remediation, because contaminants are slow to diffuse from low permeability matrix blocks between permeable pathways in heterogeneous materials. Karstified limestone and fractured rock are the most difficult formations to remediate because of their heterogeneities. Clay-rich sediments are also difficult formations to remediate, in part due to the effects of heterogeneities, and in part due to low permeabilities that limit the fluid flow necessary for many remedial techniques. Several methods have been developed to heat or fracture

clay sediments, but little headway has been made on methods for remediating karst or fractured rock.

Important secondary factors related to geologic conditions include perched water and the presence of organic-rich sediments. Organic-rich sediments retard recovery or bioavailability by sorbing contaminants, and they interfere with reactive chemicals, particularly oxidants, used to degrade contaminants. Perched water can defy remediation by many vadose zone techniques unless the locations of the perched zones can be identified.

Remarkably high concentrations of some contaminants can be remediated, but even modest concentrations of other compounds may challenge the best remedial capabilities. The presence of NAPL in the vadose zone increases the degree of difficulty, but NAPL with low vapor pressures are particularly difficult to remediate. Contaminants with a low vapor pressure and Henry's constant, and high  $K_{oc}$  and  $K_{ow}$ , are the most difficult to remediate when they occur in the vadose zone. Many compounds with a high molecular weight meet those criteria. NAPL mixed with toxic metals represent contaminant conditions that are most taxing to current remedial capabilities.

Access issues go hand-in-hand with problems associated with heterogeneity and low permeability. These problems are addressed by accessing the formation with closely spaced wells, but the cost of drilling many wells is prohibitive. New methods for creating vertical wells using direct push techniques have reduced costs, and directional drilling and hydraulic fracturing methods have improved performance during subsurface access. Many of the aggressive technologies are unsuitable in close proximity to buildings.

A variety of factors other than those related to technology performance also present major barriers to site remediation. Three important factors are rooted in the uncertainty regarding the outcome of the remedial process. The performance of many remedial methods under a variety of site conditions is uncertain; many of the evaluations cited above are based upon expected performance rather than field data. Moreover, the site conditions that characterize the regions underlying many contaminated sites are not completely known. In addition, we are uncertain as to how to assess the benefits of a particular remedial process, that is, to answer the question: "how clean is clean enough?" It is not surpris-

ing that managers are reluctant to commit the resources to move ahead with remediation in the face of these uncertainties.

These issues are certainly challenging, but they are far from insurmountable. There are three fundamental areas where additional research could fill significant gaps in current capabilities.

1. Demonstrations of remedial technology at the pilot-scale
2. Methods for monitoring and assessing remedial technology performance
3. Modeling fate and transport to evaluate risk of contaminants remaining after remediation

Pilot-scale field tests of remedial technologies under controlled conditions can provide the data needed to anticipate performance. Several *groundwater* remediation technologies have recently been tested and monitored in detail at Hill Air Force Base in Utah, and Dover Air Force Base in Delaware, under the Strategic Environmental Research and Development (SERDP) program jointly sponsored by the U.S. Environmental Protection Agency, Department of Defense, and DOE. A focused program, similar to the SERDP program, would provide essential data documenting the capabilities and limitations of technology in the vadose zone.

A research effort designed to improve methods for characterizing the vadose zone would improve capabilities by guiding the selection and design of remedial techniques. Moreover, improved monitoring and assessment capabilities would go a long way toward optimizing and controlling the implementation of any remediation method.

The fate and transport associated with contaminants that remain in the vadose zone after remediation has received little study, so it is currently unclear how much contamination can remain in the vadose zone and still have an acceptable risk. Theoretical modeling tools to make these types of predictions, which are currently available, are described in Chapter 5. The monitoring methods needed to validate such modeling efforts are among the suite of tools that is needed to characterize the vadose zone under any circumstances. Research into this issue would provide important guidance on how to prioritize remedial resources, where to evaluate remedial performance, and when to conclude that remediation is complete.

## REFERENCES

- Adenekan, A.E. 1992. "Numerical modeling of multiphase transport of multi-component organic contaminants and heat in the subsurface." *Ph.D. dissertation*, University of California, Berkeley.
- Adenekan, A.E., T.W. Patzek, and K. Pruess. 1993. "Modeling of multiphase transport of multicomponent organic contaminants and heat in the subsurface: numerical model formulation." *Water Resources Research*, 29(11): 3727-3740.
- Ahlers, C. F., S. Finsterle, and G. S. Bodvarsson. 1998. "Characterization and prediction of subsurface pneumatic pressure variations at Yucca Mountain." in *Proceedings of the TOUGH Workshop '98, LBNL 41995, CONF 980559*, Lawrence Berkeley National Laboratory, Berkeley, CA. May 4-6.
- Aiken, B. 1992. "Horizontal wells are cost-effective for *in situ* air stripping." *Ground Water Monitoring Review*, 12(3): 55.
- Alfoldi, L. 1988. "Groundwater microbiology: problems and biological treatment-state-of-the-art report." *Wat. Sci. Tech.*, 20:1-31.
- Anderson, T. A., E. A. Guthrie, and B. T. Walton. "Phytoremediation." *Environ. Sci. Tech.*, 27: 2630-2636.
- Anderson, T.A. and J.R. Coats. 1994. "Bioremediation Through Rhizosphere Technology." *ACS Symposium Series 563*, American Chemical Society, Washington, D.C.
- Anon. 1985. "Land Ban." *Federal Register*, Washington, D.C., 50(105): 23250-23258.
- Arafat, H., V. Hebatpuria, H. Rho, N. Pinto, P. Bishop, and R. Buchanan. (In Press). "Immobilization of Phenol in Cement-Based Solidified/Stabilized Hazardous Wastes Using Regenerated Activated Carbon: Role of Carbon." *Journal of Hazardous Materials*.
- Armstrong, J.E., E.O. Frind, and R.D. McClellan. 1994. "Nonequilibrium mass transfer between the vapor, aqueous, and solid phases in unsaturated soils during vapor extraction." *Water Resources Research*, 30(2): 355-368.
- Arndt, D. 1981. *Manganese Compounds as Oxidizing Agents in Organic Chemistry*. Open Court Pub. Co., LaSalle, IL.
- Auer, L. H., N. D. Rosenberg, K. H. Birdsell, and E. M. Whitney. 1996. "The effects of barometric pumping on contaminant transport." *J. Contaminant Hydrol.*, 24(2): 145-162.



Baehr, A.L. and G.E. Hoag. 1988. "A modeling and experimental investigation of induced venting of gasoline-contaminated soils" in *Soil Contaminated by Petroleum*, John Wiley and Sons, New York, NY: 113-123.

Baehr, A.L. and C.J. Joss, 1995. "An updated model of induced airflow in the unsaturated zone." *Water Resources Research*, 31(2): 417-421.

Baibakov, N.K. and A.R. Garushev. 1989. *Thermal Methods of Petroleum Production*. Elsevier, New York, NY.

Baker, K. H. and D. S. Herson. 1990. "In situ bioremediation of contaminated aquifers and subsurface soils." *Geomicrobiol. J.*, 8:133-146.

Barbeni, M., C. Nfinero, E. Pelizzetti, E. Borgarello, and N. Serpone. 1987. "Chemical Degradation of Chlorophenols with Fenton's Reagent." *Chemosphere*, 16: 2225-37.

Basel, M.D. 1991. "Two-dimensional propagation of steam through partially saturated porous media." *Ph.D. dissertation*, University of California, Berkeley.

Battelle. 1993. *Technical Resources Document on Solidification/Stabilization and Its Application to Waste Materials*. USEPA, Cincinnati, OH.

Bellamy, W.D., P.A. Hickman, and N. Ziemba. 1991. "Treatment of VOC-contaminated Groundwater by Hydrogen Peroxide and Ozone Oxidation." *Res. Journal WPCF*, 63: 120-28.

Bishop, P. 1988. "Leaching of Inorganic Hazardous Constituents from Stabilized/Solidified Hazardous Wastes." *Hazardous Wastes & Hazardous Materials*, 5: 128-143.

Boberg, T.C. 1988. *Thermal Methods of Oil Recovery*. John Wiley and Sons, New York, NY.

Bowers, A.R., P. Gaddipati, W.W. Eckenfelder, and R.M. Monsen. 1989. "Treatment of Toxic or Refractory Wastewaters with Hydrogen Peroxide." *Wat. Sci. Tech.*, 21: 477-86.

Brown, R.A., C. Nelson, and M.C. Leahy. 1997. "Combining Oxidation and Bioremediation for the Treatment of Recalcitrant Organics." *In Situ and On-Site Bioremediation*. Battelle Press, Columbus, OH: 4(4): 457-462.

Brunsing, T.P. 1987. "The block displacement method field demonstration and specifications." *U.S. EPA Project Summary*, 600-S2-87-023: 1-6.

Brusseau, M.L. 1991. "Transport of organic chemicals by gas advection in structured or heterogeneous porous media: Development of a model and application to column experiments." *Water Resources Research*, 27(12): 3189-3199.

Buckingham, E. "Contributions to our knowledge of the aeration of soils." *U.S. Department of Agriculture Bureau of Soils Bulletin*, 25(7) 1904.

Burger, J., P. Sourieau, and M. Combarous. 1985. *Thermal Methods of Oil Recovery*. Gulf Publishing, Paris.

Burken, J.G. and J.L. Schnoor. 1998. "Predictive relationships for uptake of organic contaminants by hybrid poplar trees." *Environmental Science and Technology*, 32: 3379-3385.

Caldwell, R., P. Cote, and C. Chao. 1990. "Investigation of Solidification for the Immobilization of Trace Organic Contaminants." *Hazardous Wastes & Hazardous Materials*, 7: 273-282.

Carter, E.E. 1997. "Progress in forming bottom barriers under waste sites." in *Proceedings of the International Containment Technology Conference and Exhibition*, Feb. 9-12, 1997, St. Petersburg, FL: 431-437.

Cartledge, F. K., H.C. Eaton, and M.E. Tittlebaum. 1990. "The Morphology and Microchemistry of Solidified/Stabilized Hazardous Waste Systems." *Project Summary*, USEPA, EPA/600/S2-89/056.

Case, T. L. 1997. "Reactive Permanganate Grouts for Horizontal Permeable Barriers and *In Situ* Treatment of Groundwater." *M.S. thesis*, Colorado School of Mines, Golden, CO.

Clark, W. E. 1967. "Computing the barometric efficiency of a well." *Journal of Hydraulics Division*, in *Proceedings of the American Society of Civil Engineers*, HY4, 93.

Clayton, W. S. and C. H. Nelson. 1995. "*In Situ* Sparging: Managing Chemical Transport and Mass Transfer." in *Proceedings of the 1995 Superfund Conference and Exhibition*, E. J. Krause and Assoc., Bethesda, MD.

Clayton, W.S. 1998. "Ozone and Contaminant Transport During *In Situ* Ozonation" in *Physical, Chemical, and Thermal Technologies, Remediation of Chlorinated and Recalcitrant Compounds*. G.B. Wickramanayake and R.E. Hinchee, (Eds.), Battelle Press, Columbus, OH: 389-395

Clements, W. E. and M. H. Wilkening. 1974. "Atmospheric pressure effects on Rn-222 transport across the earth-air interface." *Journal of Geophysical Research*, 79(33): 5025.

Cline, S.R., O.R. West, N.E. Korte, F.G. Gardner, R.L. Siegrist, and J.L. Baker. 1997. "KMnO<sub>4</sub> Chemical Oxidation and Deep Soil Mixing for Soil Treatment." *Geotechnical News*, December: 25-28.

Conner, J. 1990. *Chemical Fixation and Solidification of Hazardous Wastes*. Van Nostrand Reinhold, New York, NY.

Conner, J., A. Li, and S. Cotton. 1990. "Stabilization of Hazardous Waste Land-fill Leachate Treatment Residue." in *Proceedings of the Gulf Coast Hazardous Substance Research Center Symposium on Solidification/Stabilization*, Beaumont, TX: 6-14.

Conner, J. R. 1995. "Recent Findings in Immobilization of Organics as Measured by Total Constituent Analysis." *Waste Management*, 15(5/6): 359-369.

Cusack, F., S. Singh, C. McCarthy, J. Grieco, M. Derocco, D. Nguyen, H. Lappinscott, and J. W. Costerton. 1992. "Enhanced oil-recovery - 3-dimensional sandpack simulation of ultramicrobacteria resuscitation in reservoir formation." *J. Gen. Microbiol.*, 138: 647-655.

Davidson, D. T., J.B. Sheeler, and N.G. Delbridge. 1958. *Highway Research Board Bulletin*, 193: 31-32.

Davis, E. L. 1997. "How Heat Can Enhance *In Situ* Soil and Aquifer Remediation: Important Chemical Properties and Guidance on Choosing the Appropriate Technique." *Ground Water Issue*, U.S. Environmental Protection Agency, EPA/540/S-97/502, April.

Davis, L.C., M.K. Banks, A.P. Schwab, M. Narayanan, L.E. Erickson and J.C. Tracy, 1998a. *Plant-based bioremediation*. In *Bioremediation: Principles and Practice, Vol 2. Biodegradation Technology Developments*. S.K. Sikdar and R.L. Irvine, (Eds.), Technomic Publishing Co., Lancaster, PA: 183-219.

Davis, L.C., S. Vanderhoof, J. Dana, K. Selk, K. Smith, B. Goplen, and L.E. Erickson. 1998b. "Chlorinated solvent movement through plants monitored by Fourier transform infrared (FTIR) spectroscopy." *Journal of Hazardous Substance Research*, 1(4): 1-26.

Davis, P.M. 1983. "Surface deformation associated with a dipping hydrofracture." *J. Geop. Res.*, 88: 5826-5834.

Davis-Hoover, W., T. Bryndzia, M. Roulier, L. Murdoch, M. Kemper, P. Cluxton, S. Al-Abed, B. Slack, and S. Vesper. 1999. "In Situ Bioremediation Utilizing Horizontal Lasagna", *In Situ and On Site Bioremediation Symposium*, April, 1999, San Diego, CA.

Deflaun, M.F., B.M. Marshall, E.P. Kulle and S.B. Levy. 1994. "Tn5 insertion mutants of *Pseudomonas fluorescens* defective in adhesion to soil and seeds." *Applied and Environmental Microbiology* 60:2637-2642

De Voe, C. and K.S. Udell. 1998. "Thermodynamic and Hydrodynamic Behavior of Water and DNAPLs During Heating." *Remediation of Chlorinated and Recalcitrant Compounds: Nonaqueous-Phase Liquids*. Battelle Press, Columbus, OH.

DOE. 1996. "In Situ Enhanced Soil Mixing." *Innovative Technology Summary Report*, U.S. Department of Energy, Office of Science and Technology, Washington, D.C.

Dreiling, D.N., L.G. Henning, R.D. Jurgens, and D.L. Ballard. 1998. "Multi-site Comparison of Chlorinated Solvent Remediation Using Innovative Technology." in *Proceedings from the First Int. Conf. on Remediation of Chlorinated and Recalcitrant Compounds*, May, 1998, Monterey, CA.

Du, Y., A. Aydin, and L.C. Murdoch. 1993. "Incremental growth of a shallow hydraulic fracture at a waste remediation site, Oakbrook, Illinois from inversion of elevation changes." *Int. J. Rock Mech. Min. Sci.*, 30(7): 1273-1279.

EPA. 1995a. "Bioventing Principles and Practice, Volume I: Bioventing Principles." *EPA/540/R-95/534a*, U. S. Environmental Protection Agency, Washington, D.C.

EPA. 1995b. "Principles and Practices of Bioventing, Volume II: Bioventing Design." *EPA/540/R-95/534a*, U. S. Environmental Protection Agency, Washington, D.C.

Eddy, C. A., B. B. Looney, J. M. Dougherty, T. C. Hazen, and D. S. Kaback. 1991. *Characterization of the geology, geochemistry, hydrology and microbiology of the in-situ air stripping demonstration site at the Savannah River Site*. Westinghouse Savannah River Company, WSRC-RD-91-21.

El-Korchi, T., D. Gress, K. Baldwin, and P. Bishop. 1989. "Evaluating the Freeze-Thaw Durability of Portland Cement Stabilized/Solidified Hazardous Waste Using Acoustic Measurements." *Environmental Aspects of Stabilization and Solidification of Hazardous and Radioactive Wastes*, American Society for Testing and Materials, Philadelphia, PA, ASTM STP 1033: 184-191.

Ellerd, Michael G., J. W. Massman, D. P. Schwaegler, and V. J. Rohay. 1999. "Enhancements for passive vapor extraction: the Hanford study." *Groundwater*, 37(3): 427.

Erickson, L.E. 1997. "An overview of research on the beneficial effects of vegetation in contaminated soil." *Annals of the New York Academy of Sciences*, 829: 30-35.

Erickson, L.E., L.C. Davis, and M. Narayanan. 1995. "Bioenergetics and bioremediation of contaminated soil." *Thermochimica Acta*, 250: 353-358.

Escher, E. D., and J.P. Newton. 1985. *The Determination of Fixation Treatment Method Limits for Hazardous Waste Liquids and Industrial Sludges*. USEPA, EPA/160019-85/25.

Fairbanks, H. A. 1896. "Notes on a breathing gas well." *Science*, 3: 693.

Falta, R.W. (1996) “A program for analyzing transient and steady-state soil gas pump tests, *Ground Water*, 34(4), 750-755.

Falta, R.W., I. Javandel, K. Pruess, and P.A. Witherspoon. 1989. “Density-driven flow of gas in the unsaturated zone due to the evaporation of volatile organic compounds.” *Water Resources Research*, 28(2): 323-335.

Falta, R.W., K. Pruess, I. Javandel, and P.A. Witherspoon. 1992a. “Numerical modeling of steam injection for the removal of nonaqueous phase liquids from the subsurface, 1. numerical formulation.” *Water Resources Research*, 28(2): 433-449.

Falta, R.W., K. Pruess, I. Javandel, and P.A. Witherspoon. 1992b. “Numerical modeling of steam injection for the removal of nonaqueous phase liquids from the subsurface, 2. code validation and application.” *Water Resources Research*, 28(2): 451-465.

Falta, R.W., K. Pruess, S. Finsterle, and A. Battistelli. 1995. *T2VOC user's guide*. Lawrence Berkeley Laboratory Rep. LBL-36400 UC-400.

Fanale, F. P., W. B. Banerdt, R. S. Saunders, L. A. Johansen, and J. R. Salvail. 1982. “Seasonal carbon dioxide exchange between the regolith and atmosphere of Mars: Experimental and theoretical studies.” *Journal of Geophysical Research*, 87(B12): 10215-10225.

Fisher, S. 1992. *Wupatki Ruins Trail Guide*, Southwest Parks and Monuments Association, Tucson, AZ.

Flathman, P.E. and G.R. Lanza. 1998. “Phytoremediation: Current views on an emerging green technology.” *Journal of Soil Contamination*, 7: 415-432.

Fluor Daniel GTI. 1998. *Draft In Situ Ozonation Technology Demonstration Project Report for Remediation of PCP and PAHs in Soil and Groundwater, Ecodyne Pond Site, Windsor, California*.

Forbes, J., J. Havlena, M. Burkhard, and K. Myers. 1993. “Monitoring of VOCs in deep vadose zone using multi-port soil gas wells and multi-port soil gas / ground water wells.” in *Proceedings from the Seventh National Outdoor Action Conference*, Las Vegas, NV.

Forsyth, P.A. 1994a. “A positivity preserving method for simulation of steam injection for NAPL site remediation.” *Adv. Water Resour.*, 16: 351-370.

Forsyth, P.A. 1994b. “Three-dimensional modeling of steam flush for DNAPL site remediation.” J. Numer. (Int.), *Methods Fluids*, 19: 1055-1081.

Forsyth, P.A., and B.Y. Shao. 1991. “Numerical simulation of gas venting for NAPL site remediation.” *Adv. Water Resour.*, 14(6): 354-367.

Frank, U., N. Barkley. 1995. "Remediation of low permeability subsurface formations by fracturing enhancement of soil vapor extraction." *Journal of Hazardous Materials*, 40: 191-201.

Fredrickson, J. K., R. J. Hicks, S. W. Li, and F. J. Brockman. 1988. "Plasmid incidence in bacteria from deep subsurface sediments." *Appl. Environ. Microbiol.*, 54:2916-2923.

Furth, A.J., G.K. Burke, and W.L. Deutsch. 1997. "Use of jet grouting to create a low permeability horizontal barrier below an incinerator as landfill." in *Proceedings of the International Containment Technology Conference and Exhibition*, Feb. 9-12, 1997, St. Petersburg, FL: 499-505.

Garbesi, K., R. Sextro, W. J. Fisk, M. P. Modera, and K. L. Revzan. 1993. "Soil-gas entry into an experimental basement: model measurement comparisons and seasonal effects." *Environ. Sci. Technol.*, 27: 466.

Gates, D.D., and R.L. Siegrist. 1993. *Laboratory Evaluation of Chemical Oxidation Using Hydrogen Peroxide. Report from The X-231B Project for In Situ Treatment by Physicochemical Processes Coupled with Soil Mixing*. Oak Ridge National Laboratory. ORNL/TM-12259.

Gates, D.D., and R.L. Siegrist. 1995. "In Situ Chemical Oxidation of Trichloroethylene Using Hydrogen Peroxide." *ASCE Journal of Environ. Engineering*, 121: 639-44.

Gates, D.D., R.L. Siegrist, and S.R. Cline. 1995. "Chemical Oxidation of Contaminants in Clay or Sandy Soil." in *Proceedings of ASCE National Conference on Environmental Engineering*. Am. Soc. of Civil Eng., Pittsburgh, PA.

Gauglitz, P.A., J.S. Roberts, T.M. Bergsman, S.M. Caley, W.O. Heath, M.C. Miller, R.W. Moss, and R. Schalla. 1994. "Six-Phase Soil Heating Accelerates VOC Extraction from Clay Soil." *Presented at Spectrum '94: International Nuclear and Hazardous Waste Management*, Atlanta, Georgia, August 14-18, 1994.

Gierke, J.S., C. Wang, O.R. West, and R.L. Siegrist. 1995. "In Situ Mixed Region Vapor Stripping: 3. Model Development and Application." *Environmental Science & Technology*, 29(9): 2208-2216.

Gierke, J.S., N.J. Hutzler, D.B. McKenzie. 1992. "Vapor transport in unsaturated soil columns: Implications for vapor extraction." *Water Resources Research*, 28(2): 323-335.

Gierke, J.S. and S.E. Powers. 1997. "Increasing implementation of *in situ* treatment technologies through field-scale performance assessments." *Water Environment Research*, 69(2): 196-205.

Grathwohl, P. 1998. *Diffusion in Natural Porous Media: Contaminant Transport, Sorption/Desorption and Dissolution Kinetics*. Kluwer Academic Publishers, Boston, MA.

Harkness, M. R., J. B. McDermott, D. A. Abramowicz, J. J. Salvo, W. P. Flanagan, M. L. Stephens, F. J. Mondello, R. J. May, J. H. Lobos, K. M. Carroll, M. J. Brennan, A. A. Bracco, K. M. Fish, G. L. Warner, P. R. Wilson, D. K. Dietrich, D. T. Lin, C. B. Margan, and W. L. Gately. 1993. "In situ stimulation of aerobic PCB biodegradation in Hudson River sediments." *Science*, 259: 503-507.

Hazen, T. C. 1997. "Bioremediation." in: *Microbiology of the Terrestrial Subsurface*, P. Amy and D. Haldeman (Eds.), CRC Press, Boca Raton, FL: 247-266.

Hazen, T. C. 1999a. "Critical Biogeochemical Parameters Used for In Situ Bioremediation of Solvents in Fractured Rock." in *Proceedings from Dynamics of Fluids in Fractured Rocks*, LBNL-42718, Berkeley, CA: 169-171.

Hazen, T. C. 1999b. "Case Study: Full-scale in situ bioremediation demonstration (methane biostimulation) of the Savannah River Site Integrated Demonstration Project." in: *Bioremediation of Contaminated Soils*, D. C. Adriano and J. M. Bollag, (Eds.), Monograph of the Soil Science Society of America/American Society of Agronomy.

Hazen, T. C., K. H. Lombard, B. B. Looney, M. V. Enzien, J. M. Dougherty, C. B. Fliermans, J. Wear, and C.A. Eddy-Dilek. 1997. "Full Scale Demonstration of In Situ Bioremediation of Chlorinated Solvents In the Deep Subsurface Using Gaseous Nutrient Biostimulation." *Progress in Microbial Ecology*: 597-604.

Hebatpuria, V. 1998. "Leaching of Organic Hazardous Wastes from Stabilized/Solidified Hazardous Wastes," M.S., *University of Cincinnati*, Cincinnati, OH.

Hebatpuria, V. M., Arafat, H. A., Bishop, P. L., and Pinto, N. G. (In Press-a). "Leaching Behavior of Selected Aromatics in Cement-Based Solidification/Stabilization Under Different Leaching Conditions." *Environmental Engineering Science*.

Hebatpuria, V. M., H.A. Arafat, H. Rho, P.L. Bishop, N.G. Pinto, and R. Buchanan. (In Press-b). "Immobilization of Phenol in Cement-Based Solidified/Stabilized Hazardous Wastes Using Regenerated Activated Carbon: Leaching Studies." *Journal of Hazardous Materials*.

Helmig, R., C. Braun, and M. Emmert. 1994. *MUFTE-A Numerical Model for Simulation of Multiphase Flow Processes in Porous and Fractured-Porous*

*Media*. Programmdokumentation (HG 208), Technical Report 94/3, Institute für Wasserbau, Universität Stuttgart.

Heron, G., T.H. Christensen, T. Heron, T.H. Larsen. 1998. "Thermally Enhanced Remediation at DNAPL Sites: The Competition Between Downward Mobilization and Upward Volatilization." *Remediation of Chlorinated and Recalcitrant Compounds: Nonaqueous-Phase Liquids*. Battelle Press, Columbus, OH.

Hiller, D. and H. Gudemann. 1989. "Analysis of vapor extraction data from applications in Europe." in *Proceedings of Third International Conference on New Frontiers for Hazardous Waste Management*, EPA/600/8-89/072, Pittsburgh, PA, September 10-13, 1989.

Hinchee, R. E., D. C. Downey, and T. Beard. 1989. "Enhancing biodegradation of petroleum hydrocarbon fuels through soil venting." in *Proceedings of the Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water: prevention, detection and restoration*, Houston, TX, Nov 15-17, 1989: 235-248

Hodgman, C. D. 1952. *Handbook of Chemistry and Physics*, 34th ed., Chemical Rubber Publishing Co., Cleveland, OH.

Hoigne, J. and H. Bador. 1983. "Rate Constants of Reaction of Ozone with Organic and Inorganic Compounds in Water." *Water Research*, 17: 173.

Hoigne, J., and H. Bader. 1976. "The role of hydroxyl radical reactions in ozonation processes in aqueous solutions." *Water Res.*, 10: 377-386.

Holbrook, T.M., D.H. Bass, P.M. Boersma, D.C. DiGiulio, J.J. Eisenbeis, N.J. Hutzler, E.P. Roberts. 1998. *Vapor Extraction and Air Sparging*. American Academy of Environmental Engineers, Annapolis, MD.

Horvath, R. S. 1972. "Microbial co-metabolism and the degradation of organic compounds in nature." *Bacteriol*, 36:146-155.

Huguenin, R. L. 1982. "Chemical weathering and the Viking biology experiment on Mars." *Journal of Geophysical Research*, 87(B12): 10069-10082.

Hunt, J.R., N. Sitar, and K.S. Udell. 1988. "Nonaqueous phase liquid transport and cleanup, 2, experimental studies." *Water Resources Research*, 24(8): 1259-1269.

Hutzler, N.J., B.E. Murphy, J.S. Gierke. 1989. *State of Technology Review: Vapor Extraction Systems*. EPA 600/2-89-024.

Huyakorn, P.S., S. Panday, and Y.S. Wu. 1994. "A three-dimensional multiphase flow model for assessing NAPL contamination in porous and fractured media, I, formulation." *J. Contam. Hydrol.*, 16: 109-130.



Iben, I.E.T. et al. 1995. "Thermal Blanket for In-Situ Remediation of Surficial Contamination: A Pilot Test." *Environmental Science and Technology*, 30(11).

Jarosch, T., R. J. Beleski, and D. Faust. 1994. *Final Report: In Situ Radio Frequency Heating Demonstration*. Westinghouse Savannah River Company, Savannah River Site, Aiken, SC, WSRC-TR-93-673.

Jerome, K.M., Riha, B., and Looney, B.B. 1997. *Demonstration of In Situ Oxidation of DNAPL Using the Geo-Cleanse Technology*. WSRC-TR-97-00283. Westinghouse Savannah River Company, Aiken, SC.

Johnson, P.C., M.W. Kemblowski, J.D. Colthart. 1990a. "Quantitative analysis for the cleanup of hydrocarbon-contaminated soils by *in situ* soil venting." *Ground Water*, 28(3): 413-429.

Johnson, P.C., C.C. Stanley, M.W. Kemblowski, D.L. Byers, J.D. Colthart. 1990b. "A practical approach to the design, operation, and monitoring of *in situ* soil-venting systems." *Ground Water Monitoring Review*, 10(2): 159-178.

Jordan, D.L., J.W. Mercer, R.M. Cohen. 1995. *Review of Mathematical Modeling for Evaluating Soil Vapor Extraction Systems*, EPA/540/R-95/513.

Kasevich, R., R. Holmes, D. Faust, and R. Beleski. 1993. "Radio frequency heat enhances contaminant removal." *Soils*, March 18, 1993.

Keet, B. A. 1995. "Bioslurping State of the Art." *in: Applied Bioremediation of Petroleum Hydrocarbons*. R. E. Hinchee, J. A. Kittel, and H. J. Reisinger, (Eds.), Battelle Press, Columbus, OH: 329-334.

Knauss, K.G., R.D. Aines, M.J. Dibley, R.N. Leif, and D.A. Mew. 1997. *Hydrous phyrolysis/oxidation: in-ground thermal destruction of organic contaminants*. Lawrence Livermore National Laboratory, UCRL-JC-126636.

Kruger, E.L., T.A. Anderson, and J.R. Coats. 1997. "Phytoremediation of Soil and Water Contaminants." *ACS Symposium Series 664*, American Chemical Society, Washington, D.C.

Kyles, J. H., K.C. Malinowski, and T.F. Stanczyk. 1987. "Solidification/ Stabilization of Hazardous Waste: A Comparison of Conventional and Novel Techniques." *in Proceedings of the 19th Mid Atlantic Industrial Waste Conference*, J. C. Evans, (Ed.), Technomic Press, Lancaster, PA: 554-569.

Lake, L.W. 1989. *Enhanced Oil Recovery*. Prentice Hall, Englewood Cliffs, NJ.

Lear, P. R. and J.R. Conner. 1992. "Immobilization of Low Level Organic Compounds in Contaminated Soils." *Hydrocarbon Contaminated Soils*, P. T. Kostecki, E. J. Calabrese, and M. Bonazountas, (Eds.), Lewis Publishers, Boca Raton, FL: 459-485.

Leeson, A. and R. E. Hinchee. 1996. *Soil Bioventing : Principles and Practice*. Lewis Publishers, New York, NY.

Leif, R.N., M. Chiarappa, R.D. Aines, R.L. Newmark, K.G. Knauss, and C. Eaker. 1998. "In situ hydrothermal oxidative destruction of DNAPLs in a creosote-contaminated site." In *Physical, Chemical and Thermal Technologies, Remediation of Chlorinated and Recalcitrant Compounds*. Wickramanayake and Hinchee, (Eds.), Battelle Press, Columbus, OH: 133-138.

Leonard, R. J. and D.T. Davidson. 1959. *Highway Research Board Bulletin*, 231: 7-10.

Leung, S.W., R.J. Watts, and G.C. Miller. 1992. "Degradation of Perchloroethylene by Fenton's Reagent: Speciation and Pathway." *J. Environ. Qual.*, 21: 377-81.

Li, Z.M, *et al.* 1997. "Fenton Oxidation of 2,4,6-Trinitrotoluene in Contaminated Soil Slurries." *Environmental Engineering Science*, 14(1): 55-66.

Lin, M., and D.T. Mackenzie. 1983. *Test of Adsorbents and Solidification Techniques*. Brookhaven National Laboratory, Upton, NY.

Litchfield, C. D. 1993. *In situ bioremediation: basis and practices*. In: *Biotreatment of Industrial and Hazardous Waste*, M. A. Levin and M. A. Gealt, (Eds.), McGraw-Hill, Inc., New York, NY: 167-196.

Little, J. C., J. M. Daisey, and W. W. Nazaroff. 1992. "Transport of subsurface contaminants into buildings." *Environ. Sci. Technol.*, 26(11): 2058.

Looney, B. B., J. Rossabi, D. M. Tuck, C. L. Bergren, R. S. Van Pelt, W. E. Jones, A. E. Stevenson, and B. S. Kristiansen. 1992. *Assessing DNAPL contamination, A/M Area, Savannah River Site: Phase I results (U)*, WSRC-RP-1302, Westinghouse Savannah River Company, Aiken, SC.

Lowe, K.S., F.G. Gardner, R.L. Siegrist, and T.C. Houk. 1999. "Field Pilot Test of In Situ Chemical Oxidation through Recirculation Using Vertical Wells at the Portsmouth Gaseous Diffusion Plant." in *Proceedings from the EPA Conf. on Abiotic In-Situ Technologies for Groundwater Remediation*, August 31-September 2, 1999, Dallas TX.

Lyman, W., W. Reehl, and D. Rosenblatt. 1990. *Handbook of Chemical Property Estimation Methods*. American Chemical Society, Washington D.C.

Marine, I. W. 1975. "Water level fluctuations due to earth tides in a well pumping from slightly fractured crystalline rock." *Water Resour. Res.*, 11(1): 165-173.

Marvin, B.K., C.H. Nelson, W. Clayton, K.M. Sullivan, and G. Skladany. 1998. "In Situ Chemical Oxidation of Pentachlorophenol and Polycyclic Aromatic

Hydrocarbons: From Laboratory Tests to Field Demonstration.” *Proceedings of the 1st International Conf. Remediation of Chlorinated and Recalcitrant Compounds*, May 1998, Monterey, CA.

Marvin, B.K., W.S. Clayton, C.H. Nelson, K. Sullivan, and G. Skladany. 1998. “In-Situ Chemical Oxidation of Pentachlorophenol: From Laboratory Tests to Field Scale Demonstration” in *Physical, Chemical, and Thermal Technologies, Remediation of Chlorinated and Recalcitrant Compounds*. :383-388, (Eds.), G.B. Wickramanayake, and R.E. Hincsee, Battelle Press, Columbus, OH.

Massman, J. and D. F. Farrier. 1992. “Effects of atmospheric pressures on gas transport in the vadose zone.” *Water Resour. Res.*, 28(3): 777.

McCullough, J., T. C. Hazen, S. M. Benson, F. B. Metting, and A. C. Palmisano. 1999. *Bioremediation of Metals and Radionuclides. What it is and how it works*. LBNL-42595, Berkeley, CA.

Means, J. L., L.A. Smith, K.W. Nehring, S.E. Brauning, A.R. Gavaskar, B.M. Sass, C.C. Wiles, and C.I. Mashni. 1995. *The Application of Solidification/Stabilization to Waste Materials*. Lewis Publishers, Boca Raton, FL.

Menegus, D.K. and K.S. Udell. 1985. “A study of steam injection into water saturated capillary porous media. Heat Transfer in Porous Media and Particulate Flows.” *ASME HTD*, 46: 151-157.

Michaelson, G. 1993. *Guidance for Design, Installation and Operation of Soil Venting Systems*. PUBL-SW185-93, Emergency and Remedial Response Section, Wisconsin Department of Natural Resources, Madison, WI.

Miller, C.A. 1975. “Stability of moving surfaces in fluid systems with heat and mass transfer - III: stability of displacement fronts in porous media.” *AIChE Journal*, 21: 474-479.

Montgomery, D. M. 1989. “Organophilic Clays in the Stabilization/Solidification of Hazardous Wastes.” *Ph.D. dissertation*, Imperial College, London.

Montgomery, D., C. Sollars, R. Perry, S. Tarling, P. Barnes, and E. Henderson. 1991a. “Treatment of Organic-Contaminated Industrial Wastes Using Cement-Based Stabilization/Solidification - I. Microstructural Analysis of Cement-Organic Interactions.” *Waste Management and Research*, 9: 103-111.

Montgomery, D., C. Sollars, R. Perry, S. Tarling, P. Barnes, and E. Henderson 1991b. “Treatment of Organic-Contaminated Industrial Wastes Using Cement-Based Stabilization/Solidification - II. Microstructural Analysis of the Organophilic Clay as a Pre-Solidification Adsorbent.” *Waste Management & Research*, 9: 113-125.

- Mortland, M.M., S. Shaobai, and S.A. Boyd. 1986. "Clay-organic complexes as adsorbants for phenol and chlorophenols." *Clay and clay minerals*, 34(5): 581-585.
- Murdoch, L., B. Slack, B. Siegrist, S. Vesper, and T. Meiggs. 1997b. "Hydraulic Fracturing Advances." *Civil Engineering*. May, 1997: 10A-12A.
- Murdoch, L.C. 1995. "Forms of hydraulic fractures created during a field test in fine-grained glacial drift." *Quarterly Journal of Engineering Geology*, 28: 23-35.
- Murdoch, L.C. 1995. "Hydraulic and impulse fracturing for low permeability soils." *Chapter in Petroleum Contaminated Low Permeability Soil*, American Petroleum Institute Publication: 4631.
- Murdoch, L.C., G. Losonsky, P. Cluxton, B. Patterson, I. Klich, B. Braswell. 1991. *The Feasibility of Hydraulic Fracturing of Soil to Improve Remedial Actions*. Final Report, EPA600/2-91-012, NTIS Report PB91-181818.
- Murdoch, L.C., D. Wilson, K. Savage, W. Slack, and J. Uber. 1994. *Alternative Methods for Fluid Delivery and Recovery*. USEPA/625/R-94/003.
- Murdoch, L.C., W. Slack, R. Siegrist, S. Vesper, and T. Meiggs. 1997. "Advanced hydraulic fracturing methods to create *in situ* reactive barriers." in *Proceedings of the International Containment Technology Conference and Exhibition*, Feb. 9-12, 1997, St. Petersburg, FL.
- Myers, T., and M. Zappa. 1987. *Laboratory Investigation of Organic Contaminant Immobilization by Proprietary Processing of Basin F Liquid, Rocky Mountain Arsenal, Denver, Colorado*. U.S. Army Corps of Engineers, Vicksburg, MS.
- Narasimhan, T. N., Y. W. Tsang, and H. Y. Holman. 1990. "On the potential importance of transient air flow in advective radon entry into buildings." *Geophysical Research Letters*, 17(6): 821.
- Narayanan, M., J.C. Tracy, L.C. Davis, and L.E. Erickson. 1998. "Modeling the fate of toluene in a chamber with alfalfa plants. 1. Theory and modeling concepts." *Journal of Hazardous Substance Research*, 1(5): 1-39.
- Narayanan, M., J.C. Tracy, L.C. Davis, and L.E. Erickson. 1998b. "Modeling the fate of toluene in a chamber with alfalfa plants. 2. Numerical results and comparison study." *Journal of Hazardous Substance Research*, 1(5): 40-84.
- Narayanan, M., L.E. Erickson, and L.C. Davis. 1999. "Simple plant-based design strategies for volatile organic pollutants." *Environmental Progress*, In Press.

Narayanan, M., N.K. Russell, L.C. Davis, and L.E. Erickson. 1996. "Experimental and modeling studies of the fate of trichloroethylene in a chamber with alfalfa plants." *Proceedings of the HSRC/WERC Joint Conference on the Environment*, Kansas State University, Manhattan, KS: 474-481.

Narayanan, Muralidharan. 1998. "Modeling the Movement and Fate of Contaminants in an Experimental Chamber with Alfalfa Plants." *Ph.D. dissertation*, Kansas State University, Manhattan, KS.

National Research Council. 1993. *In Situ Bioremediation: When does it work?* National Academy Press, Washington, D.C.

NATO. 1998. *NATO/CCMS Pilot Study Special Session on Treatment Walls and Permeable Reactive Barriers*. EPA 542-R-98-003.

Nelson, C.H. and R.A. Brown. 1994. *Adapting Ozonation for Soil and Ground Water Cleanup. Chemical Engineering*. McGraw-Hill, Inc.

Nelson, C.H., M. Seaman, D.M. Peterson, S. Nelson, and R. Buschbom. 1997. "Ozone Sparging for the Remediation of MGP Contaminants." *In Situ and On-Site Bioremediation: Volume 3*. fourth International *In Situ* and On-Site Bioremediation Symposium, :457-462. Battelle Press, Columbus, OH.

Newmark, R.L. (Ed.) 1992. *The interim engineering report, Lawrence Livermore National Laboratory*. Report No. UCRL-ID-110064.

Newmark, R.L. (Ed.) 1994. *Dynamic underground stripping demonstration project, LLNL gasoline spill demonstration report*. Lawrence Livermore National Laboratory, UCRL-ID-116964.

Newmark, R.L. and R.D. Aines. 1997. *Dumping pump and treat: rapid cleanups using thermal technology*. Lawrence Livermore National Laboratory, UCRL-JC 126637 Preprint.

Nilson, R. H., E. W. Peterson, K. H. Lie, N. R. Burkhard, and J. R. Hearst. 1991. "Atmospheric pumping: a mechanism causing vertical transport of contaminated gases through fractured permeable media." *Journal of Geophysical Research*, 96(B13): 21933.

Nitao, J.J. 1993. *Reference Manual for the NUFT Flow and Transport Code*. Version 1.0, Lawrence Livermore National Laboratory Report.

Ong, S.K. and L. Lion. 1991. "Mechanisms for Trichloroethylene Vapor Sorption onto Soil Minerals." *J. Environ. Qual*, 20: 180-188.

Ong, S.K., L.W. Lion, and C.A. Shoemaker. 1992. "Effects of soil moisture and physical-chemical properties of organic pollutants on vapor-phase transport in the vadose zone." *J. of Contam. Hydrol.*, 11(1992): 273-290.

Owczarski, P. C., D. J. Holford, H. D. Freeman, and G. W. Gee. 1990. "Effects of changing water content and atmospheric pressure on radon flux from surfaces of five soil types." *Geophysical Research Letters*, 17(6): 817.

Panday, S., P.A. Forsyth, R.W. Falta, Y.S. Wu, and P.S. Huyakorn. 1995. "Considerations for robust compositional simulations of subsurface nonaqueous phase liquid contamination and remediation." *Water Resources Research*, 31(5): 1273-1298.

Paul, E. A. and F. G. Clark. 1989. *Soil microbiology and Biochemistry*. Academic Press, San Diego, CA.

Peck, A. J. 1960. "The water table as affected by atmospheric pressure." *Journal of Geophysical Research*, 65(8): 2383.

Peramaki, M.P. 1993. "Soil-vapor extraction system piping design and blower selection: A spreadsheet program." *Proceedings of the Seventh National Outdoor Action Conference and Exposition on Aquifer Restoration, Ground Water Monitoring and Geophysical Methods, Ground Water Management Book 15*, May 25-27, 1993, Las Vegas, NV: 15-29.

Peurrung, L. M. and R. Schalla. 1998. *Six-Phase Soil Heating of the Saturated Zone. Remediation of Chlorinated and Recalcitrant Compounds: Physical, Chemical, and Thermal Technologies*. Battelle Press, Columbus, OH.

Phelan, J.M., B. Reavis, J. Swanson, W. Cheng, H. Dev, and J. Enk. 1997. *Design, Demonstration and Evaluation of a Thermal Enhanced Vapor Extraction System*. Sandia National Laboratories, Albuquerque, NM, SAND97-1251.

Pirkle, R. J., D. E. Wyatt, V. Price, and B. B. Looney. 1992. "Barometric pumping: the connection between the vadose zone and the atmosphere." *The Focus Eastern Regional Ground Water Issues Conference*.

Pollard, S. J., C.J. Sollars, and R. Perry. 1990. "The Reuse of Spent Bleaching Earth for the Stabilization/Solidification of Mixed Waste Streams." *Environmental Technology*, 11(12): 1113-1122.

Prats, M. 1982. *Thermal Recovery*. Society of Petroleum Engineers, Dallas, TX.

Qiu, Y., M. Zappi, C. Kuo, and E. Fleming. 1999. "Kinetic and Mechanistic Study of Ozonation of Three Dichlorophenols in Aqueous solution." *Journal of Environmental Engineering*, :441-450.

Ravikmur, J.X. and M. Gurol. 1994. "Chemical Oxidation of Chlorinated Organics by Hydrogen Peroxide in the Presence of Sand." *Environ. Sci. Technol.*, 28: 394-400.

Riaz, M., and E. Zamorani. 1989. "A Study on the Effects of 1,3,5-Trichlorobenzene Solidified Cement." *Cement and Concrete Research*, 19: 124-130.

Rice, R.G., and M.E. Browning. 1980. "Ozone for Industrial Water and Wastewater Treatment." *EPA Report No. 600/2-80-060*, April, 1980. U.S. Environmental Protection Agency, Robert L. Kerr Environmental Research Laboratory, Ada, OK.

Riha, B. D., and J. Rossabi. 1997. "Miscellaneous Chemical Basin treatability study: An analysis of passive soil vapor extraction wells (PSVE)." *WSRC-TR-97-00405*, Westinghouse Savannah River Company, Aiken, SC.

Ripp, S., D. E. Nivens, R. Bulage, and G. S. Sayler. 1999. *Field-scale bioremediation monitoring utilizing bioluminescent genetically engineered microorganisms*. In: *Bioremediation Technologies for Polycyclic Aromatic Hydrocarbon Compounds*. Battele Press.

Ritzi Jr., R. W., S. Sorooshian, and P. A. Hsieh. 1991. "The estimation of fluid flow properties from the response of water levels in wells to the combined atmospheric and earth tide forces." *Water Resour. Res.*, 27(5): 1929.

Robinson, A. L. and R. G. Sextro 1995. "Direct measurement of soil-gas entry pressure into an experimental basement driven by atmospheric pressure fluctuations." *Geophysical Research Letters*, 22(14): 1803.

Rohay, V. J., and R. J. Cameron. 1992. "Field measurements of natural soil-gas venting cycles in boreholes at the Hanford Site, Washington." *Eos Transactions*, American Geophysical Union 1992 Fall Meeting, 73(43): 238.

Rojstaczer, S., and F. S. Riley. 1990. "Response of the water level in a well to earth tides and atmospheric loading under unconfined conditions." *Water Resour. Res.*, 26(8): 1803.

Rojstaczer, S. 1988. "Determination of fluid flow properties from the response of water levels in wells to atmospheric loading." *Water Resour. Res.*, 24(11): 1927.

Rossabi, J., B. B. Looney, C. A. Eddy-Dilek, B. D. Riha, and V. J. Rohay. 1994. "Passive remediation of chlorinated volatile organic compounds using barometric pumping." in *Proceedings of the Water Environment Federation: Innovative Solutions for Contaminated Site Management*, March 6-9, Miami, FL: 377-388.

Rossabi, J. 1999. "The influence of atmospheric pressure variations on subsurface soilgas and the implications for environmental characterization and remediation." *Ph.D. thesis*, Clemson University, University of Michigan Press.

- Roy, K.A. 1990. "In Situ Detoxifier." *HAZMAT WORLD*, Tower-Borner Publishing, Inc. Glen Ellyn, IL.
- Santharam, S.K., L.E. Erickson, and L.T. Fan. 1994. "Modeling the fate of polynuclear aromatic hydrocarbons in the rhizosphere." in *Proceedings of the 9th Annual Conference on Hazardous Waste Remediation*, Kansas State University, Manhattan, KS: 333-350.
- Sass, I., O. Caldonazzi, T. deBeyer. 1997. "The application of flowmontana for environmental problems." in *Proceedings of the International Containment Technology Conference and Exhibition*, Feb. 9-12, St. Petersburg, FL: 489-498.
- Schnarr, M., C. Truax, G. Farquhar, E. Hood, T. Gonully, and B. Stickney. 1998. "Laboratory and Controlled Field Experimentation Using Potassium Permanganate to Remediate Trichloroethylene and Perchloroethylene DNAPLs in Porous Media." *Journal of Contaminant Hydrology*, 29: 205-224.
- Schnoor, J. L., L. A. Licht, S. C. McCutcheon, N. L. Wolfe, and L. H. Carreira. 1995. "Phytoremediation of organic and nutrient contaminants." *Environ. Sci. Tech.*, 29: 318A-323A.
- Schnoor, J.L. 1997. *Design of phytoremediation at contaminated sites. Advances in Innovative Groundwater Remediation Technologies*. Groundwater Remediation Technologies Analysis Center, Pittsburgh. PA.
- Schnoor, J.L., L.A. Licht, S.C. McCutcheon, N.L. Wolfe, and L.H. Carreira. 1995. "Phytoremediation of organic and nutrient contaminants." *Environmental Science and Technology*, 29: 318A-323A.
- Shan, C. 1995. "Analytical solutions for determining vertical air permeability in unsaturated soils." *Water Resour. Res.*, 31(9): 2193.
- Shan, C., R.W. Falta, and I. Javendal. 1992. "Analytical solutions for steady state gas flow to a soil vapor extraction well." *Water Resources Research*, 28(4): 1105-1120.
- Sheldon, R.B. et al. 1996, "Field Demonstration of a Full-Scale In Situ Thermal Desorption System for the Remediation of Soil Containing PCBs and Other Hydrocarbons." *HAZWaste World Superfund XVII*, Washington, D.C., October 15-17.
- Sheriff, T. S., C.J. Sollars, D. Montgomery, and R. Perry. 1989. "The Use of Activated Charcoal and Tetra-Alkylammonium-Substituted Clays in Cement-Based Stabilization/Solidification of Phenols and Chlorinated Phenols." *Environmental Aspects of Stabilization and Solidification of Hazardous and Radioactive Wastes*, P. L. Cote and T. M. Gilliam, (Eds.), American Society for Testing and Materials, Philadelphia, PA: 273-286.



Sherman, B.M., H.E. Allen, and C.P. Huang. 1998. "Catalyzed Hydrogen Peroxide Treatment of 2,4,6-Trinitrotoluene in Soils." in *Proceedings from the 13th Mid-Atlantic Industrial and Hazardous Waste Conference*, Technomic Publishers, Lancaster, PA.

Siegrist, R. L., K.S. Lowe, L.C. Murdoch, W.W. Slack, and T.C. Houk. 1998. "X-231A Demonstration of *in situ* remediation of DNAPL compounds in low permeability media by soil fracturing with thermally enhanced mass recovery and reactive barrier destruction." *DOE Report ORNL/TM-13534*.

Siegrist R.L., K. S. Lowe, L.C. Murdoch, T.L. Case, and D.A.Pickering. 1999. "In situ oxidization by fracture emplaced reactive solids." *Jour of Environ. Eng.*, 125(5): 429-440.

Siegrist, R.L. 1998. "In Situ Chemical Oxidation: Technology Features and Applications." *Invited presentation at the Conference on Advances in Innovative Groundwater Remediation Technologies*, December 15, 1998, U.S. EPA Technology Innovation Office, Washington, D.C.

Siegrist, R.L. and J.J. van Ee. "1994. Measuring and Interpreting VOCs in Soils: State of the Art and Research Needs." *EPA/540/R-94/506*, U.S. EPA ORD, Washington, D.C. 20460.

Siegrist, R.L. K.S. Lowe, L.C. Murdoch, T.L. Case, D.A. Pickering, and T.C. Houk. 1998b. "Horizontal Treatment Barriers of Fracture-Emplaced Iron and Permanganate Particles." *NATO/CCMS Pilot Study Special Session on Treatment Walls and Permeable Reactive Barriers*, EPA 542-R-98-003. May 1998: 77-82.

Siegrist, R.L., K.S. Lowe, L.C. Murdoch, and A.M. Struse. 1999. "In Situ Chemical Treatment Using Hydraulic Fracturing to Emplace Fe<sub>0</sub> Metal and KMnO<sub>4</sub> Reactive Solids." in *Proceedings from the Conf. on Abiotic In-Situ Technologies for Groundwater Remediation*, August 31-September 2, 1999, Dallas TX.

Siegrist, R.L., K.S. Lowe, L.C. Murdoch, T.L. Case, and D.A. Pickering. 1999. "In Situ Oxidation by Fracture Emplaced Reactive Solids." *J. Environmental Engineering*, 125(5): 429-440.

Siegrist, R.L., K.S. Lowe, L.C. Murdoch, W.W. Slack, and T.C. Houk. 1998a. "X-231A Demonstration of *In Situ* Remediation of DNAPL Compounds in Low Permeability Media by Soil Fracturing with Thermally Enhanced Mass Recovery or Reactive Barrier Destruction." *Oak Ridge National Laboratory Report*, March, ORNL/TM-13534.

Siegrist, R.L., M.A. Urynowicz, and O.R. West. 1999. "An Overview of *In Situ* Chemical Oxidation Technology Features and Applications." in *Proceedings*

from *Conf. on Abiotic In-Situ Technologies for Groundwater Remediation*, August 31-September 2, 1999, Dallas TX.

Siegrist, R.L., M.A. Urynowicz, and O.R. West. 1999. "An Overview of In Situ Chemical Oxidation Technology Features and Applications." in *Proceedings from Conf. on Abiotic In-Situ Technologies for Groundwater Remediation*, August 31-September 2, 1999, Dallas TX.

Siegrist, R.L., M.I. Morris, O.R. West, D.D. Gates, and D.A. Pickering, et al. 1993. "Full-scale Demonstration of Physicochemical Processes for In Situ Treatment of Contaminated Soil." in *Proceedings from Waste Management '93*, March, 1993. Tucson, AZ, U.S. Department of Energy.

Siegrist, R.L., N.E. Korte, D. Smuin, O.R. West, D.D. Gates, and J.S. Gundersen. 1996. "In Situ Treatment of Contaminants in Low Permeability Soils: Biogeochemical Enhancement by Subsurface Manipulation." in *Proceedings from First Int. Conf. on Contaminants in the Soil Environment in the Australasia-Pacific Region*, February, 1996, Adelaide.

Siegrist, R.L., N.E. Korte, K.S. Lowe, and O.R. West. 1999. "Permeation Dispersal of Treatment Agents for In Situ Remediation: 1. Field Trials to Compare Multiple Reagents." *Final project report for U.S. Department of Energy by Oak Ridge National Laboratory*, Oak Ridge, TN. ORNL/TM.

Siegrist, R.L., O.R. West, M.I. Morris, D.A. Pickering, D.W. Greene, C.A. Muhr, D.D. Davenport, and J.S. Gierke. 1995a. "In Situ Mixed Region Vapor Stripping of Low Permeability Media. 2. Full Scale Field Experiments." *Environmental Science & Technology*, 29(9): 2198-2207.

Siegrist, R.L., S. R. Cline, T.M. Gilliam, and J.R. Conner. 1995b. "In Situ Stabilization of Mixed Waste Contaminated Soil." in *Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes*, T.M. Gilliam and C.C. Wiles (Eds.), STP 1240. ASTM, West Conshohocken, PA: 667-684.

Siegrist, R.L., O.R. West, M.I. Morris, D.A. Pickering, D.W. Greene, C.A. Muhr, D.D. Davenport, and J.S. Gierke. 1995. "In situ mixed region vapor stripping in low-permeability media. 2. Full-scale field experiments." *Environmental Science & Technology*, 29(9):2198-2207.

Sleep, B. E., and J. F. Sykes. 1989. "Modeling the transport of volatile organics in variably saturated media." *Water Resour. Res.*, 25(1): 81, 1989.

Smith, L.A. and R. E. Hinchey. 1993. *In situ thermal technologies for site remediation*. Lewis Publishers, CRC Press, FL.

Smith, R. C. 1979. "The Effect of Organics on Pozzolanic Reactions." *Internal Report 57*, IU Conversion Systems, Inc., Philadelphia, PA.

Sonntag, R.E. and G. van Wylen. 1982. *Introduction to Thermodynamics, Classical and Statistical*. John Wiley, New York, NY.

Stavnes, S., C. A. Yorke, and L. Thompson. 1996 “In situ bioremediation of petroleum in tight soils using hydraulic fracturing.” *HazWaste World/Superfund XVII Conference*, October 16, 1996, Washington, D.C.

Stegemeier, G. L. and H.J.Vinegar. 1995. “Soil Remediation By Surface Heating and Vacuum Extraction,” *SPE 29771, SPE/EPA Exploration and Production Environmental Conference*, March 27-29, 1995, Houston, TX.

Stewart, L.D., and K.S. Udell. 1988. “Mechanisms of residual oil displacement by steam injection.” *SPE Reservoir Engineering*, 3 (November): 1233-1242.

Stewart, L.D., and K.S. Udell. 1989. “The effects of gravity and multiphase flow on the stability of condensation fronts in porous media.” *Multiphase Transport in Porous Media*, ASME HTD-127.

Stewart, L.D., J. Gin, and S. Hicken. 1998. “Field demonstration of thermally enhanced extraction for DNAPL source removal.” In *Nonaqueous Phase Liquids, Remediation of Chlorinated and Recalcitrant Compounds*. Wickramanayake and Hinchee, (Eds.), Battelle Press, Columbus, OH: 211-216.

Stinson, M.K. and S. Sawyer. 1989. “In Situ Stabilization/Solidification of PCB-Contaminated Soil.” in *Proceedings from the Third Intern. Conf. on New Frontiers for Hazardous Waste Management*, September, 1989, Pittsburgh, PA: 151-159.

Stoval, S.L. 1934. “Recovery of oil from depleted sands by means of dry steam.” *Oil Weekly*, 73: 17-24.

Struse, A.M. 1999. “Mass Transport of Potassium Permanganate in Low Permeability Media and Matrix Interactions.” *M.S. thesis*, Colorado School of Mines, Golden, CO.

Thomas, J. M., and C. H. Ward. 1989. “In situ bioremediation of organic contaminants in the subsurface.” *Environ. Sci. Technol.*, 23: 760-766.

Thomas, J. M., and C. H. Ward. 1992. “Subsurface microbial ecology and bioremediation.” *J. Haz. Mat.*, 32: 179-194.

Thorne, D. J., and J.D. Watt 1965. “Composition and Pozzolanic Properties of Pulverized Fly Ash.” *Journal of Applied Chemistry*, 15: 595-604.

Thornton, S.I., Parker, D.G., and White, D.N., in *Proceedings of the 4<sup>th</sup> International Fly Ash Utilization Symposium*, U.S. Bureau of Mines, Denver, CO, 1975.

Tittlebaum, M., H. Eaton, F. Cartledge, M. Walsh, and A. Roy. 1986. "Procedures for Characterizing Effects of Organics on Solidification/Stabilization of Hazardous Wastes." *Hazardous and Industrial Solid Waste Testing and Disposal*, R. Conway, (Ed.), American Society for Testing and Materials, Philadelphia, PA: 308-318.

Trapp, Stefan and J. Craig McFarlane, (Eds.). 1995. *Plant Contamination*. CRC Press, Inc., Boca Raton, FL.

Treweek, G.P. and J. Wogec. 1988. "Soil Remediation by Air/Steam Stripping." in *Proceedings from the Fifth National Conference, Hazardous Wastes and Hazardous Materials*: 147-153.

Tsang, Y. W., and T. N. Narasimhan. 1992. "Effects of periodic atmospheric pressure variation on radon entry into buildings." *Journal of Geophysical Research*, 97(B6): 9161.

Tyre, B.W., R.J. Watts, and G.C. Miller. 1991. "Treatment of Four Biorefractory Contaminants in Soils Using Catalyzed Hydrogen Peroxide." *J. Environ. Qual.*, 20: 832-38.

U.S. EPA. 1991. "Soil Vapor Extraction Technology Reference Handbook." *EPA/540/2/91/003*.

U.S. EPA. 1995. "Remediation Case Studies: Soil Vapor Extraction." *EPA-542-R-95-004*.

U.S. EPA. 1997. "Analysis of Selected Enhancements for Soil Vapor Extraction." *EPA542R97007*, National Service Center for Environmental Publications, Cincinnati, OH.

U.S. EPA. 1998. "Remediation Case Studies: *In Situ* Soil Treatment Technologies (Soil Vapor Extraction, Thermal Processes)." Volume 8, *EPA-542-R-98-012*.

U.S. EPA. 1995a. "KAI Radio Frequency Heating Technology. SITE Technology Capsule." U.S. Environmental Protection Agency, *EPA 540/R-94/528a*, January 1995.

U.S. EPA. 1995b. "IIRTI Radio Frequency Heating Technology. SITE Innovative Technology Evaluation Report." U.S. Environmental Protection Agency, *EPA 540/R-94/527*, June, 1995.

U.S. EPA. 1993. "Consistent Implementation Of the FY 1993 Guidance on Technical Impracticability of Groundwater Restoration at SUPERFUND Sites." Department of Commerce, National Technical Information Service 5285 Port Royal Rd Springfield, VA 22151 Order Number: EPA540F95001.

U.S. EPA. 1989. "Records of Decision Analysis of Superfund Sites Employing Solidification/Stabilization as a Component of the Selected Remedy." *USEPA*, Washington, D.C.

U.S. EPA. 1993. "Solidification/Stabilization of Organics and Inorganics." *Engineering Bulletin*, USEPA, EPA/540/S-92/015.

U.S. EPA. 1994. "Records of Decision Analysis of Superfund Sites Employing Solidification/Stabilization as a Component of the Selected Remedy." *USEPA*, Washington, D.C.

U.S. EPA. 1989. "Bioremediation of hazardous waste sites workshop." *CERI-89-11*. Washington, DC.

U.S. EPA. 1998. "*In Situ* Remediation Technology: *In Situ* Chemical Oxidation." *EPA 542-R-98-008*. Office of Solid Waste and Emergency Response, Washington, D.C.

Udell, K.S. 1994. *Heat and mass transfer in cleanup of toxic waste, Advances in Heat Transfer Research*. C.L. Tien, (Ed.), Environmental and Engineering Geophysical Society, Englewood, CO: 195-211.

Udell, K.S., and L.D. Stewart. 1989. "Field study of in situ steam injection and vacuum extraction for recovery of volatile organic solvents." Sanitary Engineering and Environmental Health Research Laboratory, University of California, Berkeley, *UCB-SEEHRL Report No. 89-2*.

Unger, A.J.A., E.A. Sudicky, and P.A. Forsyth. 1995. "Mechanisms controlling vacuum extraction coupled with air sparging for remediation of heterogeneous formations contaminated by dense nonaqueous phase liquids." *Water Resources Research*, 31(6): 1913-1925.

Urynowicz, M. and R.L. Siegrist. 1999. "Permeation Dispersal of Treatment Agents for *In Situ* Remediation: 2. Intact Core Experiments with Chemical Oxidants." *Final project report for Oak Ridge National Laboratory by Colorado School of Mines*, Golden, CO.

Vaughan, P.J., K.S. Udell, and M.J. Wilt. 1993. "The effects of steam injection on the electrical conductivity of an unconsolidated sand saturated with a salt solution." *J. Geophysical Res.*, 98(B1): 509-518.

Vella, P.A. and B. Veronda. 1994. "Oxidation of Trichloroethylene: A Comparison of Potassium Permanganate and Fenton's Reagent. 3rd Intern." Symposium on Chemical Oxidation, in *In Situ Chemical Oxidation for the Nineties*, Technomic Publishing Co., Inc. Lancaster, PA, 3: 62-73.

Vella, P.A., G. Deshinsky, J.E. Boll, J. Munder, and W.M. Joyce. 1990. "Treatment of Low Level Phenols with Potassium Permanganate." *Res. Jour. WPCF*, 62(7): 907-14.

Venkatadri, R. and R.W. Peters. 1993. "Chemical Oxidation Technologies: Ultraviolet Light/Hydrogen Peroxide, Fenton's Reagent, and Titanium Dioxide Assisted Photocatalysis." *J. Haz. Waste Haz. Materials*, 10(2): 107-149.

Vesper, S. J., L.C. Murdoch, S. Hayes, and W.J. Davis-Hoover. 1994. "Solid oxygen source for bioremediation in subsurface soils." *Journal of Hazardous Materials*, 36: 265-274.

Vinegar, H.J. et al. 1997. "In Situ Thermal Desorption (ISTD) of PCBs," *HAZWaste World Superfund XVIII*, Washington, D.C., December 2-4.

Vinegar, H.J. et al. 1997, "Remediation of Deep Soil Contamination Using Thermal Vacuum Wells," *SPE 39291*, Soc. Pet. Eng. Annual Technical Conference, October 5-8, San Antonio, TX.

Vinegar H.J., E.P. de Rouffignac, G.L. Stegemeier, J.M. Hirsch, and F.G. Carl. 1998. "In Situ Thermal Desorption Using Thermal Wells and Blankets." Wickramanayake, G.B. and Hinchee R.E., "Physical, Chemical and Thermal Technologies," 1998 The First International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, California, May 18-21.

Vinegar, H.J., G.L. Stegemeier, E.P. de Rouffignac, and C.C. Chou. 1994. "Vacuum Method for Removing Soil Contaminants Utilizing Thermal Conduction Heating," *U.S. Patent Nos. 5,190,405*, issued March 2, 1993, and *5,318,116*, issued June 7, 1994.

Vroblesky, D.A., C.T. Nietch, and J.T. Morris. 1999. "Chlorinated ethenes from groundwater in tree trunks." *Environmental Science and Technology*, 33: 510-515.

Wang, Stodt, Steirman and Murdoch. "Mapping hydraulic fractures using a borehole-to-surface electrical resistivity method." *Geoexploration*, 28.

Watts, R.J. and B.R. Smith. 1991. "Catalyzed Hydrogen Peroxide Treatment of Octachlorobibenzo-pdioxin (occd) in Surface Soils." *Chemosphere*, 23: 949-55.

Watts, R.J., A.P. Jones, P. Chen, and A. Kenny. 1997. "Mineral-catalyzed Fenton-like Oxidation of Sorbed Chlorobenzenes." *Water Environ. Res.*, 69: 269-275.

Watts, R.J., S.W. Leung, and M.D. Udell. 1991. "Treatment of Contaminated Soils Using Catalyzed Hydrogen Peroxide." in *Proceedings to the First International Symposium on Chemical Oxidation*, Technomic, Nashville, TN.

Watts, R.J., P.A. Rausch, S.W. Leung, and M.D. Udell. 1990. "Treatment of Pentachlorophenol Contaminated Soils using Fenton's Reagent." *Haz. Waste and Haz. Mater.*, 7: 335-45.

Weber, D., and F. Schwill. 1991. "Passive vapor monitoring of underground storage tanks for leak detection." *Environmental Monitoring and Assessment*, 16: 99.

Weeks, E. P. 1979. "Barometric fluctuations in well tapping deep unconfined aquifers." *Water Resour. Res.*, 15(5): 1167.

Weeks, E. P. 1978. "Field determination of vertical permeability to air in the unsaturated zone." *U.S. Geological Survey Professional Paper*, 1051.

West, O.R., S.R. Cline, R.L. Siegrist, T.C. Houk, W.L. Holden, F.G. Gardner, and R.M. Schlosser. 1998. "A Field-Scale Test of *In Situ* Chemical Oxidation Through Recirculation." in *Proceedings from Spectrum '98 Intern. Conf. on Nuclear and Hazardous Waste Management*, Sept. 13-18, Denver, CO: 1051-57.

West, O.R., R.L. Siegrist, J.S. Gierke, A.J. Lucero, H.L. Jennings, and S.W. Schmunk. 1995a. "In Situ Mixed Region Vapor Stripping of Low Permeability Media. 1. Process Features and Laboratory Experiments." *Environmental Science & Technology*, 29(9): 2191-2197.

West, O.R., R.L. Siegrist, T.J. Mitchell, and R.A. Jenkins. 1995b. "Measurement Error and Spatial Variability Effects on Characterization of Volatile Organics in the Subsurface." *Environmental Science & Technology*, 29(3): 647-656.

Weston, 1992. "Rocky Mountain Arsenal *In Situ* Radio Frequency Heating/Vapor Extraction Pilot Test Report, Final, Volume I." *U.S. Army Program Manager for Rocky Mountain Arsenal Contamination Cleanup, document control number 5300-01-12-AAFP*.

White, M.D., and M. Oostrom. 1996a. "STOMP Subsurface Transport Over Multiple Phase: Theory Guide." *PNNL-11216 (UC-2010)*, Pacific Northwest National Laboratory, Richland, WA.

White, M.D., and M. Oostrom. 1996b. "STOMP Subsurface Transport Over Multiple Phase: User' Guide." *PNNL-11216 (UC-2010)*, Pacific Northwest National Laboratory, Richland, WA.

Yan, Y. and F.W. Schwartz. 1996. "*In Situ* Oxidative Dechlorination of Trichloroethylene by Potassium Permanganate." in *Proceedings from 3rd Intern. Conf. on Advanced Oxidation Technologies*,. October 26-29, Cincinnati, OH.

Yuan, Z.G., and K.S. Udell. 1993. "Steam distillation of a single component hydrocarbon liquid in porous media." *Int. J. Heat Mass Transfer*, 36(4): 887-897.

Zachary, S. P. 1993. "In-situ active/passive bioreclamation of vadose zone soils contaminated with gasoline and waste oil using soil vapor extraction/bioventing." in *Proceedings of the Meeting on Petroleum Hydrocarbons and organic chemicals in groundwater: prevention, detection, and restoration*, Nov 10-12, Houston, TX: 509-521.

Zwick, T., R. E. Hinchee, R. Hoeppel, C. Kyburg, and L. Bowling. 1994. "Passive bioventing driven by natural air exchange." in *Proceedings of the 1994 Petroleum hydrocarbons and organic chemicals in groundwater conference*, November 2-4, Houston, TX.